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An Investigation of the Adsorption of Gases by Wood and its Components and of Gas Adsorption Techniques as a Means of Studying the Area and Structure of Pulp and Paper

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AN INVESTIGATION OF THE ADSORPTION OF GASES BY WOOD AND ITS COMPONENTS AND OF GAS ADSORPTION TECHNIQUES AS A MEANS OF STUDYING THE AREA AND STRUCTURE OF PULP AND PAPER

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TABLE OF CONTENTS

INTRODUCTION AND PRESENTATION OF THE PROBLEM

It is generally recognized that a strong interrelationship exists between the external surface area of pulp fibers and many of the properties of both the pulp itself and the paper into which it is made. The external specific surface, in addition to being a measure of the potential area of the fibers available for bonding, markedly influences the drainage characteristics and is closely related to the ability of pulps to retain dyes, fillers, sizing materials, and beater additives. In paper, the exposed surface or the unbonded area influences a number of properties such as opacity, reflectance, porosity, and retention of printing inks. The bonded area of paper, on the other hand, is probably the most important single factor contributing to the strength of the sheet.

It is not surprising, therefore, that considerable attention has been given to area characteristics of pulp and paper. In the past few years, microscopic, solute adsorption, permeability, surface catalytic, and optical methods have been applied to estimate the external specific surface of pulp fibers with varying degrees of success. In combination, these last two methods also provide the only practical way presently available for estimating the bonded area of paper. The work which has been done in this field has dealt largely with or has made use of the wet external surface area of the pulp. Little attention has been given to the dry external specific surface of the fibers or to the direct measurement of the bonded and unbonded area of paper. A method which has been suggested for such area measurements involves gas adsorption. The several studies of the adsorption of gas on pulp, cotton, and paper which have been made were brief and mainly exploratory in nature. They have indicated, however, that if properly applied, gas

adsorption techniques may provide a valuable tool for the investigation of the area and structure of dry pulp fibers, and the bonded and unbonded area of sheets of paper.

Before these applications of gas adsorption can be undertaken, it is necessary that the nature of the adsorption process be thoroughly understood; for, if gaseous adsorption data are to be of use for such studies, it is essential that only physical adsorption occurs. This is imperative since, if the gas combines chemically, is absorbed, or alters the original condition of the pulp or paper, it is of little value for area and structure investigations. Therefore, it was the aim of the initial portion of the present work to study the nature of the adsorption of several of the most promising gases i.e. nitrogen, n-butane, and carbon dioxide near their normal liquefaction (or solidification) temperature on wood and its components. From the shape of the adsorption and desorption isotherms, the equilibrium considerations, and the thermodynamics involved, a fundamental understanding of the adsorption of these three gases may be obtained. In this way, sufficient information can be made available to evaluate the usefulness of gas adsorption techniques for area and structure investigations and to determine the merits of each gas for use with cellulosic materials.

Following this work, the internal area and submicroscopic structure of wood cellulose will be investigated using gas adsorption methods. A study will be undertaken of the dry external surface area of bleached pulp fibers and the bonded and unbonded area of pulp handsheets. This work should provide valuable information on the internal and external surface characteristics of pulp fibers and should lead to a better understanding of the measurement of the bonded area of paper.

TABLE I

NOMENCLATURE

(summary of the more important symbols)

A_g	Avogadro's number, moles^{-1}
A_x	constant associated with Harkins-Jura equations, ml.(S.T.P.)/g.
E	energy of activation, kg.-cal./mole
E_1	average heat of adsorption of first adsorbed layer of gas associated with the B.E.T. equation, kg.-cal./mole
E_L	heat of liquefaction of the adsorbate, kg.-cal./mole
L	molecular cross-sectional area of the adsorbate, sq. A.
R	corrected radius calculated from a modified Kelvin adsorption equation associated with Wheeler-Shull technique, A.
R_g	gas constant, ergs/mole or cal./mole, per ^{o}K.
S	specific surface of adsorbent, sq. m./g.
T	absolute temperature, ^{o}K.
V	molar volume of adsorbate, ml.(S.T.P.)/mole
V_a	molar volume of liquefied adsorbate, ml./mole
a	specific surface associated with Fu-Bartell method, sq. cm./g.
c	constant in B.E.T. equations, dimensionless
k	empirical constant associated with the Harkins-Jura method, sq. m./ml.(S.T.P.)
n	number of layers of adsorbed gas associated with B.E.T. method
p	equilibrium gas pressure, mm. of mercury
p_o	saturation vapor pressure of the adsorbate, mm. of mercury

TABLE I (Continued)

NOMENCLATURE

(summary of the more important symbols)

$\underline{t}$	multilayer thickness of adsorbed gas at pressure $\underline{p}$, A.
$\underline{v}$	volume of adsorbed gas, ml.(S.T.P.)
$\underline{v}_g$	volume of adsorbed gas per gram of adsorbent, ml.(S.T.P.)/g.
$\underline{v}_m$	volume of gas required to form a monolayer on the adsorbent, ml. (S.T.P.)
$\underline{v}_s$	volume of gas adsorbed at saturation pressure, ml.(S.T.P.)
$\Delta\underline{F}$	change in free surface energy, ergs/sq. cm.
$\Delta\underline{H}$	differential heat of adsorption, kg.-cal./mole
α	correction factor to account for deviation of adsorbate from perfect gas laws, dimensionless
γ	surface or interfacial tension, ergs/sq. cm.
φ	decrease in free surface energy associated with Fu-Bartell equation, ergs/sq. cm.

HISTORICAL REVIEW

Investigation of the physical adsorption of gases by solids has been undertaken by many different workers during the past 125 years, and in this time extensive literature on this subject has been published. [The more important findings in this field have been the subject of a review by Brunauer (1).] Largely, this work involved only a study of the shape of adsorption isotherms, total quantities of gas adsorbed, and values of the differential heat of adsorption as computed by the Clausius-Clapeyron equation. It was not until the relatively recent development of methods for the determination of specific surface area of solids from physical adsorption measurements made near the liquefaction temperature of the gas that gas adsorption methods began to find useful application as a means of studying the structure and surface of solid materials.

This review deals first with a discussion of the methods of estimating surface area from gas adsorption data. In addition, previous work which has been reported on the adsorption of nitrogen and carbon dioxide by sprucewood, pulp, paper, and cotton is considered. Since a portion of the present research work was devoted to a study of the submicroscopic pore size distribution of wood cellulose, the Wheeler-Shull method of applying gas adsorption isotherms for this purpose is outlined. Finally, a brief summary is included of the various methods of estimating the specific surface area of pulps and the bonded area of paper which have preceded the current investigation of the usefulness of gas adsorption techniques for similar estimates.

DETERMINATION OF SPECIFIC SURFACE AREA FROM ADSORPTION ISOTHERMS

Benton and White (2), while investigating the adsorption of nitrogen on iron catalysts at liquid air temperatures, made the suggestion that certain "breaks" occurring in one of their isotherms might indicate the completion of a first and second layer of adsorbed molecules. Although later work by Emmett and Brunauer (3) showed that these "breaks" disappear when proper correction is made for the deviation of nitrogen from the perfect gas laws, Emmett (4) stated that the idea of using low-temperature van der Waals isotherms for absolute surface area measurement arose largely from the work of Benton and White.

Early successful efforts by Brunauer and Emmett (3,5,6) to utilize low-temperature adsorption data for the measurement of surface area involved an empirical method for selecting the point on the isotherm (and, therefore, the volume of gas) corresponding to the completion of a monolayer of adsorbed gas molecules. When a value was assigned for the average area covered by each adsorbed molecule, a calculation of the area of the adsorbent exposed to the gas was possible.

Brunauer, Emmett, and Teller (7) gave increased validity to the use of adsorption isotherms for area measurement by the development of a theory of multimolecular adsorption which made it possible to plot the adsorption data in such a manner as to obtain mathematically the volume of gas required to form a monolayer on a given adsorbent. The Brunauer, Emmett, and Teller (B.E.T.) theory was developed primarily to explain the common S-shaped or sigmoid isotherm although it is capable in a limiting case of reproducing a unimolecular or Langmuir adsorption curve.

The fundamental assumption of the B.E.T. multimolecular adsorption theory is that the same forces which act to cause condensation are acting to produce van der Waals adsorption. A derivation of an isotherm equation was advanced for multimolecular layers which is similar to Langmuir's (8) treatment of unimolecular adsorption.

To carry out this derivation, Brunauer, Emmett, and Teller let $\underline{s}_o$, $\underline{s}_1$, $\underline{s}_2, \cdots \underline{s}_i \cdots$ represent the surface area that is covered by only 0, 1, 2, $\cdots$ i, $\cdots$ layers of adsorbed molecules. At equilibrium $\underline{s}_o$ must remain constant, and the rate of condensation on the bare surface must be equal to the rate of evaporation from the first layer, or

$$\underline{a}_1 \underline{p} \underline{s}_o = \underline{b}_1 \underline{s}_1 e^{-\underline{E}_1/\underline{R}_g \underline{T}} \qquad (1)$$

where $\underline{p}$ is the pressure, $\underline{E}_1$ is the average heat of adsorption in the first layer, $\underline{R}_g$ is the gas constant, $\underline{T}$ the absolute temperature, e is the base of Naperian logarithms, and $\underline{a}_1$ and $\underline{b}_1$ are constants. At equilibrium, $\underline{s}_1$ also must remain constant, and it follows for the second, third, and $\underline{i}$th layers that

$$\underline{a}_2 \underline{p} \underline{s}_1 = \underline{b}_2 \underline{s}_2 e^{-\underline{E}_2/\underline{R}_g \underline{T}} \qquad (2)$$

$$\underline{a}_3 \underline{p} \underline{s}_2 = \underline{b}_3 \underline{s}_3 e^{-\underline{E}_3/\underline{R}_g \underline{T}} \qquad (3)$$

$$\underline{a}_i \underline{p} \underline{s}_{i-1} = \underline{b}_i \underline{s}_i e^{-\underline{E}_i/\underline{R}_g \underline{T}} \qquad (4)$$

where $\underline{E}_2$, $\underline{E}_3$, and $\underline{E}_i$ are the heats of adsorption in the respective layers. The total surface area of the adsorbent is given by

$$\underline{A}_s = \sum_{i=o}^{\infty} \underline{s}_i \qquad (5)$$

and the total volume adsorbed is

$$\underline{v} = \underline{v}_o \sum_{i=o}^{\infty} i\underline{s}_i \qquad (6)$$

where $\underline{v}_o$ is the volume of gas adsorbed per unit area of adsorbent surface when it is just covered with a complete unimolecular layer of adsorbed gas. It follows that

$$\underline{v}/\underline{A}_s\underline{v}_o = v/v_m = \frac{\sum_{i=o}^{\infty} i\underline{s}_i}{\sum_{i=o}^{\infty} \underline{s}_i}, \qquad (7)$$

where v_m is the volume of gas adsorbed when the entire adsorbent is covered by a unimolecular layer.

In order to carry out the summation indicated in Equation (7), it was necessary to assume that $\underline{E}_2 = \underline{E}_3 = \cdots \underline{E}_i = \underline{E}_L$ where $\underline{E}_L$ is the heat of liquefaction of the adsorbate, and that

$$\underline{b}_2/\underline{a}_2 = \underline{b}_3/\underline{a}_3 = \cdots \underline{b}_i/\underline{a}_i = \underline{g} \qquad (8)$$

where $\underline{g}$ is an appropriate constant. This is equivalent to considering that the evaporation-condensation properties of the molecules in the second and higher adsorbed layers are unaffected by the proximity of the solid and that they are the same as those in the liquid state. Next, $\underline{s}_1$, $\underline{s}_2$, $\underline{s}_3$, $\cdots$ $\underline{s}_i$ were expressed in terms of $\underline{s}_o$.

$$\underline{s}_1 = \underline{y}\underline{s}_o, \text{ where } \underline{y} = (\underline{a}_1/\underline{b}_1)\, p e^{E_1/R_gT} \qquad (9)$$

$$\underline{s}_2 = \underline{x}\underline{s}_1, \text{ where } \underline{x} = (p/g)\, e^{E_L/R_gT} \qquad (10)$$

$$\underline{s}_3 = \underline{x}\underline{s}_2 = \underline{x}^2\underline{s}_1 \qquad (11)$$

$$\underline{s}_i = \underline{x}\underline{s}_{i-1} = \underline{x}^{i-1}\underline{s}_1 = \underline{y}\underline{x}^{i-1}\underline{s}_o = \underline{c}\underline{x}^i\underline{s}_o \qquad (12)$$

where

$$\underline{c} = \underline{y}/\underline{x} = (\underline{a}_1\underline{g}/\underline{b}_1)\, e^{(E_1-E_L)/R_gT} \qquad (13)$$

Substituting for $\underline{S}_i$ in Equation (7), one obtains:

$$\underline{v} / \underline{v}_m = \frac{\underline{c}\underline{s}_o \sum_{i=1}^{\infty} i\underline{x}^i}{\underline{s}_o [1 + \underline{c} \sum_{i=1}^{\infty} \underline{x}^i]} \qquad (14)$$

The summation indicated in the denominator is the sum of an infinite geometric progression.

$$\sum_{i=1}^{\infty} \underline{x}^i = \underline{x} / (1-\underline{x}) \qquad (15)$$

and it will be noted that for the numerator

$$\sum_{i=1}^{\infty} i\underline{x}^i = \underline{x} \frac{d}{d\underline{x}} \sum_{i=1}^{\infty} \underline{x}^i = \frac{\underline{x}}{(1-\underline{x})^2} \qquad (16)$$

It therefore follows that

$$\underline{v} / \underline{v}_m = \underline{c}\underline{x} / (1-\underline{x})(1-\underline{x} + \underline{c}\underline{x}). \qquad (17)$$

If the adsorption takes place on a free surface, then at $\underline{p}_o$, the saturation vapor pressure of the liquid adsorbate, it is assumed that an infinite (actually, very large) number of layers can be built up on the adsorbent. To make $\underline{v} = \infty$ when $\underline{p} = \underline{p}_o$, $\underline{x}$ must approach unity. Then $\underline{x} = \underline{p} / \underline{p}_o$ and by substituting for $\underline{x}$ in Equation (17)

$$\underline{v} = \underline{v}_m \underline{c} \underline{p} / [\underline{p}_o - \underline{p}] [1 + (\underline{c}-1) (\underline{p} / \underline{p}_o)], \qquad (18)$$

which in a revised form

$$\underline{p} / \underline{v} (\underline{p}_o - \underline{p}) = [1 / \underline{v}_m \underline{c}] + [(\underline{c}-1) / \underline{v}_m \underline{c}] [\underline{p} / \underline{p}_o] \qquad (19)$$

constitutes the B.E.T. isotherm equation for adsorption taking place on a free

surface. The equation will, in general, yield a straight line when $p / v (p_o - p)$ is plotted against the relative pressure (p / p_o) for relative pressures between 0.05 and 0.35 if the gas-solid system gives an S-shaped isotherm (the most common case). From the slope and intercept of this plot v_m, the monolayer volume can be readily evaluated. Multiplication of the number of gas molecules corresponding to v_m by the cross-sectional area of each molecule as is indicated in Equation (20) gives the area of the solid accessible to the gas in square meters.

$$\text{Area} = A_g v_m L / 22{,}400 \times 10^{20} \qquad (20)$$

where A_g is Avogadro's number, v_m is the monolayer volume of gas in ml. (S.T.P.), and L is the molecular cross-sectional area in square Angstroms of the gas being used.

It was originally felt by Brunauer, Emmett, and Teller (7) that the nature of the constants a_1, b_1, and g, in Equation (13) were such that $a_1 g / b_1$ would not differ much from unity. This has been further studied by Davis and DeWitt (9) who, although reporting values of this fraction as high as 5 or 10, concluded that these cases are rare. The assumption of unity for this fraction appears justifiable. This makes possible the calculation of E_1, the average heat of adsorption of the gas in the first layer from a single isotherm, since

$$c = e^{(E_1 - E_L) / R_g T}. \qquad (21)$$

When the adsorbent contains extremely fine pores, adsorption does not take place on a free surface but in a limited space. At saturation, the number of adsorbed layers cannot be assumed to be infinite since they will actually be limited to a relatively small number, n. For this case, from Equation (16), one obtains instead of Equation (18)

$$v = \left\{ v_m cx / (1-x) \right\} \quad \left\{ [1-(n+1)x^n + nx^{n+1}] / [1 + (c-1)x - cx^{n+1}] \right\}. \qquad (22)$$

If $n = 1$, Equation (22) reduces to the Langmuir adsorption equation, and when $n = \infty$, Equation (19) results.

Joyner, Weinberger, and Montgomery (10) have demonstrated that when the structure of the adsorbent is such that n is limited to values less than 3 or 4, Equation (22) should be employed. For n values greater than this, the short B.E.T. Equation (19) can be used, providing the value of c for the system is considerably greater than unity. In practice, c and n are usually greater than four and Equation (19) has been found to apply to almost any isotherm between 0.05 and 0.35 relative pressure. Since outside this range it does not commonly describe the adsorption isotherm, various modifications have been suggested to extend the limits of application (11-16). In general, these modifications have dealt with revised considerations of the variation of the heat of adsorption in the second and higher layers. Therefore, they have contributed little to the improved application of the B.E.T. theory to area measurements. Equation (19) was the first and is still the most frequently employed means for the determination of specific surface area from gas adsorption data.

Harkins and Jura (17) described a method for measuring the surface area of finely divided nonporous solids which consists of measuring the heat of immersion in water after the material had picked up sufficient water vapor (several statistical layers) to cause the heat per gram of solid to be substantially independent of the amount of water adsorbed. In this manner, areas of titanium dioxide powders were obtained which were remarkably close to those calculated from nitrogen adsorption data on the same material using the B.E.T. method and 16.2 sq. A. as the area

occupied by a nitrogen molecule. This involved technique is of interest in the present discussion only because it provided a standard of surface area measurement which was used by Harkins and Jura (18) to develop a method of determining specific surface area from gas adsorption isotherms that does not require an estimation of the cross-sectional area of the adsorbate molecules.

The Harkins-Jura equations do not formulate a new theory of adsorption but are, in reality, a modified expression of the fact that the same empirical equation relating surface pressure π to the average area per adsorbed molecule σ,

$$\pi = \underline{b}_x - \underline{a}_x \sigma, \tag{23}$$

($\underline{a}_x$ and $\underline{b}_x$ are constants) that has been shown to apply to insoluble films on water, appears to apply to physically adsorbed films of gases on solids. This expression has been transformed (19) into the fugacity equation

$$\log (\underline{f} / \underline{f}_o) = \underline{B}_x - \underline{A}_x / \underline{v}_g^2 \tag{24}$$

or less accurately but more usefully to

$$\log (\underline{p} / \underline{p}_o) = \underline{B}_x - \underline{A}_x / \underline{v}_g^2 \tag{25}$$

where $\underline{A}_x$ and $\underline{B}_x$ are constants, $\underline{v}_g$ is the volume (S.T.P.) adsorbed per gram of adsorbent, and $\underline{p} / \underline{p}_o$ is the relative pressure. When $\log (\underline{p} / \underline{p}_o)$ is plotted against the reciprocal of the square of the adsorbed volume, a linear relationship is obtained for those systems where the adsorbed gas film is present in a condensed state.

The area of the solid in square inches per gram $\underline{S}$ is given by the equation

$$\underline{S} = \underline{kA}_x^{0.5}. \tag{26}$$

where A_x is the slope of a plot of Equation (25) and k is a constant whose value for nitrogen was determined using the surface area obtained from the heat of immersion of titanium dioxide previously discussed. In applying this equation to the measurement of the areas of other solids, the assumption is made that the compressibility of the physically adsorbed film is unaffected by the nature of the solid and for a given gas and temperature, that the k for one adsorbent is the same as the k for another. At the present time, the method is limited somewhat in that k has been evaluated only for krypton and nitrogen at -195.8, n-butane at 0, and n-heptane and water at 25°C.

It has frequently been found that specific surface areas calculated by the Harkins-Jura method agree quite well with those determined by the B.E.T. equation (10, 18, 20, 21). By no means, however, is agreement always observed between the area determined by the Harkins-Jura and the B.E.T. methods. Emmett (22) and Livingston (23) stated that the two equations will give a satisfactory fit to the same adsorption data and, therefore, comparable areas only if the constant c [see Equation (19)] lies between the approximate limits of 25 to 250. Regardless of the value of c, Joyner, Weinberger, and Montgomery (10) found, for porous solids, which permit maximum adsorption only a few molecules thick, that the Harkins-Jura equation could not be applied although the long B.E.T. equation was still suitable.

In the past few years, Kistler, Fischer, and Freeman (24) and Harvey (25) have each proposed methods for estimating the surface area of porous solids which assume the adsorption to be due entirely to capillary condensation superimposed upon a Langmuir monolayer. Harkins and Jura (26) demonstrated that multilayer adsorption can and usually does occur when gases are adsorbed on solids and

conclude that since the above two methods completely disregard multilayer adsorption, they are incorrect.

Recently, Fu and Bartell (27) reported a method for the measurement of the surface area of porous adsorbents which is based on the change of free surface energy occurring during adsorption. This method, like that of Harkins and Jura, does not necessitate an estimation of the molecular area of the adsorbate. When applied to adsorption measurement of porous materials, it is a fresh and apparently sound approach to the estimation of area, although as yet it does not appear to have been investigated by other workers.

Fu and Bartell believe that at temperatures not far removed from the condensation point of the gases used, adsorption on porous solids is always accompanied by condensation if the pressure is sufficiently high and if the capillaries in the material are not too small. When condensation to a liquid occurs, the original solid-vacuum surface $\underline{a}_{so}$ is replaced by a solid-liquid interface having the same area and, in addition, by a liquid-vapor surface of area $\underline{a}_{lv}$. The change in free surface energy $\Delta\underline{F}$ is

$$\Delta\underline{F} = \underline{a}_{so} (\gamma_{sl} - \gamma_{so}) + \underline{a}_{lv} \gamma_{lv}, \qquad (27)$$

where γ is the surface or interfacial tension and the nature of the interfaces is designated by the subscripts. At saturation pressure, the surface area $\underline{a}_{lv}$ term becomes essentially zero because the capillaries are completely filled with condensed liquid and the external area of porous solids is usually negligible when compared with the internal area. At saturation pressure, the total change in free surface energy is

$$\underline{a}_{so} (\gamma_{sl} - \gamma_{so}) + 0\, \gamma_{lv} = \underline{a}_{so} (\gamma_{sl} - \gamma_{so}). \qquad (28)$$

After making several assumptions as to the mechanism of adsorption in order that the Gibbs's adsorption equation may be rigorously applied, the following equation was obtained:

$$\underline{a}\varphi = \int_{n=0}^{n=n_x} \underline{n}d\mu + \int_{n=n_x}^{n=n_s} \underline{n}d\mu, \qquad (29)$$

where $\underline{a}$ is the area of the solid, φ is the decrease in free surface energy per unit area, $\underline{n}_s$ is the number of moles of vapor adsorbed at the saturation pressure, $\underline{n}_x$ is the number at pressure $\underline{p}_x$ at which liquid first forms in the capillaries, and μ is the chemical potential of the vapor.

When Equation (29) applies, $\underline{a}\varphi$ is composed of two terms: (a) the decrease of free surface energy due to the replacement of the solid-vacuum surface by a solid-liquid and a liquid-vapor interface, and (b) the decrease of the free surface energy of the liquid due to further adsorption. If this is true, a plot of $\underline{a}\varphi$ against relative pressure $\underline{p} / \underline{p}_o$ will have a composite nature. The resulting curve is generally found to be concave to the pressure axis at lower relative pressures and to become essentially a straight line as the saturation pressure is approached. An extension of these two lines to intersection gives a "break" which is thought to indicate the appearance of liquid adsorbate in the pores. The area of the solid is then obtained by

$$\underline{a} = (\underline{a}\varphi_s - \underline{a}\varphi_x) / \gamma_{lv}, \qquad (30)$$

where $\underline{a}\varphi_s$ is the total change in free surface energy at the saturation pressure and $\underline{a}\varphi_x$ is the similar change at the pressure corresponding to the "break"

mentioned above. The term γ_{lv} is the surface tension of the condensed gas which is tacitly assumed to be the same as the surface tension of the liquefied gas in the bulk phase at the same temperature.

In general, this method has been found by Fu and Bartell to give surface area values for porous materials which agree quite well with those obtained from the same adsorption data using the B.E.T. equation. Its main disadvantages are that it would not appear suitable for nonporous solids and that more adsorption data and computations are required than are necessary in applying the Harkins-Jura or the B.E.T. methods.

ADSORPTION OF NITROGEN AND CARBON DIOXIDE ON SPRUCEWOOD, PULP, PAPER, AND COTTON

Since a review of the literature has not revealed any previous work on the adsorption of n-butane by cellulosic materials, only carbon dioxide and nitrogen will be considered in so far as their adsorption on sprucewood, pulp, paper, and cotton has been investigated.

The sorption of a number of gases, including carbon dioxide, by cotton and sprucewood was studied by Grace and Maass (28). Employing gravimetric means, these workers found that, at 22°C., thoroughly dried sprucewood sorbed 0.75% of carbon dioxide at 22 cm. and 1.07% at both 42 and 76 cm. of mercury pressure. When the wood contained 3.4% moisture, however, there was no takeup of this gas. Similar work was also done with cotton, both dry and containing 5.0% of absorbed water, and no detectable sorption of carbon dioxide was noted in either case. Where sorption did take place, the gas could be readily removed by evacuation.

Salley (29) determined isotherms for the adsorption of carbon dioxide on a slightly beaten and a well beaten bleached sulfite pulp and also on untreated and mercerized cotton. Temperatures of 0 and 100°C. were used during the adsorption studies on the cotton samples, and work with the pulp was carried out at 56 and 80°C. When the adsorbent was sulfite pulp, adsorption equilibrium was reached only slowly at 80 and 56°C., and at 0°C. it could not be obtained even after prolonged exposure to the carbon dioxide. Although it was not stated directly that equilibrium was reached, the presentation of isotherms for the adsorption of carbon dioxide on the cotton samples at 0°C. indicated that this must be the case.

Nitrogen is the principal gas which has been employed for area studies with gas adsorption techniques. Emmett and DeWitt (30) were the first to study its adsorption at -195°C. on cellulosic materials. These workers investigated the adsorption of nitrogen on two specimens of paper of the type employed as insulation in telephone cables. Common S-shaped isotherms were obtained and from these the surface area accessible to the gas was computed by the B.E.T. method. The paper samples were initially evacuated at 25 and at 110°C. For those evacuated at 25°C., the calculated areas were 0.61 and 1.59 sq. m. per gram when 16.2 sq. A. was taken as the area occupied by a nitrogen molecule. In both cases, the area of similar samples desorbed at the higher temperature was substantially lower.

Assaf, Haas, and Purves (31) reported a procedure whereby a large portion of the internal area of cotton linters can be rendered accessible in a dry state. This involved soaking cotton in 10% caustic solution, neutralizing, washing, and then removing the water by successively dispersing the sample in 99+% methanol, magnesium-dried methanol, and sodium-dried benzene before drying. The nitrogen

adsorption -B.E.T. areas (molecular cross-sectional area; 17.0 sq. A) of two samples of linters treated in this way were 53.0 and 64.6 sq. m. per gram.

Rowen and Blaine (32) studied the adsorption of nitrogen at liquid nitrogen temperatures on water-dried* cotton. An S-shaped isotherm was obtained which gave a fairly linear plot between relative pressures of 0.05 and 0.30 when graphed according to the B.E.T. equation. With the assumption of 16.2 sq. A. as the cross-sectional area of a nitrogen molecule, the area of the cotton was 0.72 sq. m. per gram. When a Harkins-Jura plot of the adsorption data was prepared, a sufficient straight-line portion was not obtained to permit calculation of area by this method.

Rowen and Blaine also computed the decrease in free surface energy occurring on nitrogen adsorption employing a modification of an equation derived by Boyd and Livingston (33) from the Gibbs adsorption equation. This equation was used in the form

$$-\Delta \underline{F} = \underline{R_g T} \,/\, \underline{VS} \int_o^p (\underline{v_g} \,/\, \underline{p})\underline{dp} \qquad (31)$$

where $\underline{R_g}$ is the gas constant, $\underline{T}$ the absolute temperature, $\underline{V}$ the molar volume of the gas, $\underline{S}$ the specific surface, and $\underline{v_g}$ the volume (S.T.P.) adsorbed per gram of solid. The indicated integration when carried out graphically gave a value of 20 ergs per sq. cm. at a relative pressure of 0.40 for the adsorption of nitrogen on cotton.

* The terms, water-dried, butanol-dried, etc., have been used throughout the report to mean that the specimen was wet with the particular liquid indicated at the time it was dried.

Hunt, Blaine, and Rowen (34) have studied the areas of water-dried and benzene-dried cotton linters using nitrogen adsorption and the B.E.T. method (molecular cross-sectional area; 16.2 sq. A.). Untreated linters gave a typical S-shaped isotherm which showed no hysteresis loop on desorption and had an area of 0.6 sq. m. per gram. The isotherms for cotton samples swollen with water and with 10% caustic solution and dried from benzene following the method described by Assaf, Haas, and Purves (31) were not S-shaped but were what Brunauer, Deming, Deming, and Teller (16) have termed type IV. Instead of increasing to very large adsorbed volumes as a relative pressure of unity is approached (as would be the case if S-shaped), type IV isotherms tend toward becoming horizontal to the pressure axis. On desorption, a marked hysteresis loop resulted. Areas of 47.3 and 71.3 sq. m. per gram were obtained for the water-swollen and the alkali-swollen linters, respectively. When the alkali-treated cotton sample was conditioned to a 3.3% gain in weight by exposure to a relative humidity of 20 to 25% and evacuated at liquid nitrogen temperatures, a type IV isotherm showing hysteresis was obtained, but the measured area had been reduced to 31.6 sq. m. per gram. On further conditioning the same sample at 70 to 75% relative humidity to a weight 11.0% greater than the weight of the original sample and drying at room temperatures, the isotherm had become S-shaped, although a small hysteresis loop was still noted. The area of this latter specimen was 2.0 sq. m. per gram.

Haywood (35), as a part of a rather detailed investigation of the effect of fiber size and shape on papermaking properties, determined the surface areas of a number of hardwood ray-cell samples dried from water and dried from acetone. Low-temperature nitrogen adsorption and the B.E.T. method were used. The areas of the water-dried cells ranged from 1.1 to 3.2, whereas the same samples dried down from

acetone had areas of 3.0 to 7.1 sq. m. per gram.

Fu and Bartell (27), in order to test their method of area measurement, computed the areas of the water-dried and benzene-dried cotton linters from the adsorption data of Hunt, Blaine, and Rowen (34). The area values checked very well with those calculated by the B.E.T. method for the porous benzene-dried samples. The area of the water-dried linters, however, was 0.44 by the Fu-Bartell method as compared to a value of 0.60 sq. m. per gram by the B.E.T. equation. Fu and Bartell explained this discrepancy by stating that 0.60 sq. m. per gram was almost beyond the limit of applicability of the B.E.T. method. However, the B.E.T. method has been successfully used to measure the specific surface of numerous materials in the range of 0.10 to 0.50 sq. m. per gram (4).

DETERMINATION OF PORE SIZE DISTRIBUTION FROM GAS ADSORPTION DATA

Investigation of the pore size distribution of adsorbents has not been undertaken to any great extent. This is mainly due to the fact that until recently the only two means available for this purpose provided no more than a crude, semi-quantitative picture. These older theories, which are discussed at length by Brunauer (1), include the capillary condensation theory which permits evaluation of the pore size distribution only if it is assumed that all adsorption is due to capillary condensation, and the multimolecular adsorption theory which neglects completely any capillary condensation that takes place. Since both types of adsorption can and usually do occur when a gas is adsorbed on a porous solid at higher relative pressures, each method is only an approximation. A combination of these two theories would seem to be a logical step, and this has been done by Wheeler (36)

who recently introduced a theory which is a composite of the B.E.T. multilayer adsorption and the capillary condensation viewpoints.

WHEELER-SHULL METHOD

According to a discussion by Shull (37), the Wheeler theory may be most simply given by the equation

$$\underline{v}_s - \underline{v} = \pi \int_{\underline{R}}^{\infty} (\underline{r}-\underline{t})^2 L(\underline{r}) d\underline{r} \ . \qquad (32)$$

In this equation, $\underline{v}_s$ is the volume of gas adsorbed at saturation pressure $\underline{p}_o$, $\underline{v}$ is the volume of gas adsorbed at any intermediate pressure $\underline{p}$, $L(\underline{r})d\underline{r}$ is the total length of pores whose radii fall between $\underline{r}$ and $\underline{r} + d\underline{r}$, $\underline{R}$ is the corrected Kelvin radius which is obtained as a function of the pressure, and $\underline{t}$ is the multilayer thickness which is normally built up at pressure $\underline{p}$. The equation is a statement that the volume of gas $\underline{v}_s - \underline{v}$ not yet adsorbed at a pressure $\underline{p}$ is equal to the total volume of pores not yet filled.

The left-hand side of Equation (32) is easily obtained from the adsorption isotherm. It is desired to determine the pore size distribution function $L(\underline{r})$ which will, when integrated, show agreement with the experimental data. Prior to proceeding with this integration, however, it is necessary to evaluate $\underline{R}$ and $\underline{t}$ as functions of pressure.

To determine the corrected radius $\underline{R}$, use is made of a modified Kelvin adsorption equation in which the corrected pore radius is placed equal to the sum of the multilayer thickness and the radius normally calculated from the simple Kelvin equation. Mathematically

$$\underline{R} = \underline{t} - 2\gamma \underline{V}_a / \underline{R}_g \underline{T} (\ln \underline{p} / \underline{p}_o) \qquad (33)$$

where σ is the surface tension and the V_a the molar volume of the liquid adsorbate, R_g the gas constant per mole, and T the absolute temperature. This equation states that the radius determining the presence or absence of capillary condensation is that part of the pore not occupied due to multilayer adsorption and not that of the entire pore. The procedure for determining R, therefore, involves calculating the monolayer volume v_m from a B.E.T. plot of the adsorption isotherm and then plotting the data on a v / v_m basis against p / p_o. This is easily converted to a plot of t against p / p_o by assuming the monomolecular thickness to be 4.3 A. for nitrogen. It is now possible to employ Equation (33) to calculate the corrected Kelvin radius at various relative pressures.

Even with R known, there is not presently available a simple method of evaluation applicable to the pore size integral, Equation (32), by which the pore size distribution $L(r)$ can be obtained from numerical values of $v_s - v$. There is an indirect method, however, based on a comparison of the experimental isotherm with standard calculated isotherms which permits an easy and convenient solution of the problem.

Wheeler (36) has suggested that pore size distributions can be represented by analytical forms of the Maxwellian or Gaussian type. For a Maxwellian distribution of pore sizes

$$L(r) = Are^{-r/r_o} \qquad (34)$$

where A and r_o are constants. When this is substituted into Equation (32) and the integration performed,

$$v_s - v = Ar_o^4 M(R, r_o) \qquad (35)$$

results, where

$$M(\underline{R},\underline{r}_o) = [\pi / \underline{r}_o^{\,3}]\ [e^{-R / r_o}]\ [\underline{R}(\underline{R}-\underline{t})^2 + 6\underline{r}_o^{\,3} +$$

$$2\underline{r}_o^{\,2}(3\underline{R}-2\underline{t}) + \underline{r}\ (3\underline{R}-\underline{t})\ (\underline{R}-\underline{t})]. \qquad (36)$$

The function $M(\underline{R},\underline{r}_o)$ has been evaluated for various values of $\underline{R}$ and $\underline{r}_o$. Plots of $M(\underline{R}, \underline{r}_o)$ against $\underline{R}$ and those obtained in similar fashion for a Gaussian distribution are referred to as standard inverted isotherms and have been determined and plotted by Shull (37) for a number of different values of the parameter, $\underline{r}_o$.

For a Gaussian distribution of pore sizes

$$L(\underline{r}) = \underline{A}e^{-[(\beta / \underline{r}_o)\ (\underline{r}-\underline{r}_o)]^2} \qquad (37)$$

with $\underline{A}$, β, and $\underline{r}_o$ constants. When substituted into Equation (32), this integrates into

$$\underline{v}_s - \underline{v} = 2\underline{A}(\underline{r}_o^{\,3} / \beta)\ \ G_\beta\ (\underline{R},\underline{r}_o) \qquad (38)$$

where

$$G_\beta(\underline{R},\underline{r}_o) = \left\{ \pi /4\underline{r}_o^{\,2} \right\} \left\{ \frac{\underline{r}_o}{\beta} \quad e^{-\rho 2}\ (\underline{R}-2\underline{t} + \underline{r}_o) + \right. \qquad (39)$$

$$\left. \sqrt{\pi}[1-H(x)]\ \ [(\underline{r}_o - \underline{t})^2 + 1/2\ (\underline{r}_o / \beta)^2] \right\}$$

with $\rho = (\beta / \underline{r}_o)\ (\underline{R}-\underline{r})$ and

$$H(x) = 2/\sqrt{\pi} \int_o^x e^{-y^2}\, \underline{dy}.$$

$G_\beta(R,r_o)$ functions are available for $\beta = 2$, 5, and 10 and various values of $\underline{R}$ and $\underline{r}_o$.

The procedure for interpreting the experimental data involves first replotting the experimental isotherm as $\underline{v}_s - \underline{v}$ (log scale) against the corrected Kelvin radius $\underline{R}$. This is commonly known as an inverted isotherm. This inverted isotherm is next matched with one of the standard isotherms. If a satisfactory match is obtained, the pore size distribution can readily be computed from the parameters of the standard isotherm. Occasionally the experimental inverted isotherm cannot be fitted to one of the standard isotherms. It then becomes necessary to resolve the experimental isotherm into two or more standard isotherms (two terms are generally sufficient). For example, if an experimental isotherm can be resolved into the sum of a Maxwellian and a Gaussian standard isotherm then

$$\underline{v}_s - \underline{v} = \underline{A}_o \underline{r}_o^4 M(\underline{R},\underline{r}_o) + 2\underline{A}_1 (\underline{r}_1^3/\beta) G_{\beta_1}(R,r_1) \tag{40}$$

and hence

$$L(\underline{r}) = A_o \underline{r} e^{-r/r_o} + \underline{A}_1 e^{-\left[(\beta_1/r_1)(r-r_1)\right]^2} \tag{41}$$

Although it is the pore size distribution for a given material that is calculated, a volume distribution $V(\underline{r})$ is more generally plotted against pore diameter since this seems to have greater physical significance. The conversion is easily carried out since

$$V(\underline{r}) = \pi \underline{r}^2 L(\underline{r}) \tag{42}$$

Comparison of the distributions for different solids is best accomplished by adjusting the areas under the volume distribution curves of each to be in the same ratio as the respective total adsorptions of gas.

APPLICATIONS OF THE WHEELER-SHULL METHOD

Several applications of the method of Wheeler and Shull have been made in order to determine the pore volume distribution of porous solids. Employing nitrogen adsorption data, Shull, Elkin, and Roess (38) have investigated the microstructure of a number of silica-alumina gels. Similarly, Hunt, Blaine, and Rowen (34) made several determinations of pore volume distribution as an additional part of their studies of benzene-dried cotton linters previously discussed. When desorption isotherm data were employed, the alkali-swollen, benzene-dried cotton was shown to contain a preponderance of pores of 24 to 60 A. diameter with a peak in the distribution curve occurring at 40 A. After this material had been conditioned to a 3.3% gain in moisture and outgassed at -195°C., the area and the total pore volume had decreased, but the range of pore sizes and the location of the peak of the distribution curve were not altered. A pore volume distribution determined in the same way for the water-swollen, benzene-dried cotton ranged from 16 to 56 A. diameter with a peak at 32 A.

MEASUREMENT OF THE EXTERNAL SPECIFIC SURFACE AREA OF PULP FIBERS AND THE BONDED AREA OF PAPER

During the past twenty years, a number of methods have been investigated for the determination of the external surface area of pulp fibers. These include microscopic, solute adsorption, permeability, surface catalytic, and optical methods.

A microscopic method was employed by Graff, Schlosser, and Nihlen (39) to estimate the visible external surface of various types of pulp fibers. The adsorption of stearic acid from benzene solution by filter paper was studied by Stamm and Millett (40) as a means of measuring the external specific surface of

cellulosic materials. More recently, Beamesderfer, Thode, Chase, and Hubbard (41) employed the adsorption of Benzo Fast Scarlet dye as a measure of the surface area of unbeaten sulfite pulps. Through use of a water permeability technique, Robertson and Mason (42) and Ingmanson (43) determined the external area of wet pulp fibers. Similarly, Brown (44) estimated the exposed surface of dry pulp fibers from air permeability measurements. The method of determining the specific surface area of cellulosic materials which has been most widely used, however, is the silvering or surface catalytic technique devised by Clark (45) and subsequently modified by McEwen (46), Browning and Baker (47), and Browning (48). Optical methods utilizing the scattering of light by pulp fibers as a means for area measurement were first employed by Mason, Vivian, and Maass (49) with the object of determining the specific surface of pulp suspended in water. Although their applicability is limited, optical methods have proved extremely valuable as a means of studying the area involved in fiber-to-fiber bonding in sheets of paper.

The measurement of bonded area by optical methods was first undertaken by Parsons (50) during a study of the effect of fiber dimensions on the optical properties of a paper sheet. He employed the difference in the specific scattering coefficients of water-dried and unbonded butanol-formed pulp sheets as a measure of relative bonded area. Numerical values of bonded area were obtained but only by also using the silvering method to measure the specific surface area of the pulp. This technique was altered slightly and employed by Ratliff (51) to study the optical and surface properties of bleached kraft pulps. Van den Akker (52) suggested that better formation of the butanol sheets, and consequently more accurate bonded area values, would result if these sheets were formed from water and then the water was

displaced from the pulp by successive applications of acetone and butanol. With this modification and also with the substitution of benzene for butanol, both Keeney (53) and Leech (54) have employed the technique for bonded area studies. Other than several estimates made by Brown (44) from air permeability data, this optical method is the only means which has been employed for bonded area determinations.

EXPERIMENTAL EQUIPMENT FOR THE DETERMINATION OF ADSORPTION ISOTHERMS

The apparatus used for the determination of adsorption isotherms is of the volumetric type and is similar to that employed by Harkins and Jura (18). Its operation is based on the principle that if the pressure of gas in a buret of known volume is measured before and after adsorption on a material is allowed to take place, the quantity of gas adsorbed at the final pressure can be determined. A photograph of the equipment is given in Figure 1, and a schematic drawing is given in Figure 2.

The adsorption apparatus was constructed almost entirely of Pyrex glass. The main vacuum header extending across the top is connected at one end through a cold trap immersed in a Dry Ice-alcohol bath to the pumps and at the other end to a McLeod gage (0.005-mu minimum scale reading). Pressures of the order of 10^{-4} mm. of mercury were obtained through the use of a silicone oil (DC 703) diffusion pump backed by a Megavac rotary oil pump.

The sample to be studied is contained in adsorption bulb (A), which is sealed to the apparatus by 1-mm. capillary tubing. (The actual equipment was constructed so that two bulbs could be simultaneously evacuated but for simplification of the schematic diagram and the discussion, it is assumed that only one bulb is being utilized.) The water-jacketed gas buret (B) contains three bulbs totaling approximately 150 ml. in volume. When readings are taken, the temperature of the water in the jacket is read from thermometer (T).

The buret is connected by 2-mm. capillary tubing to the main pressure manometer M_1, behind which is mounted a meter stick. The right-hand leg of the

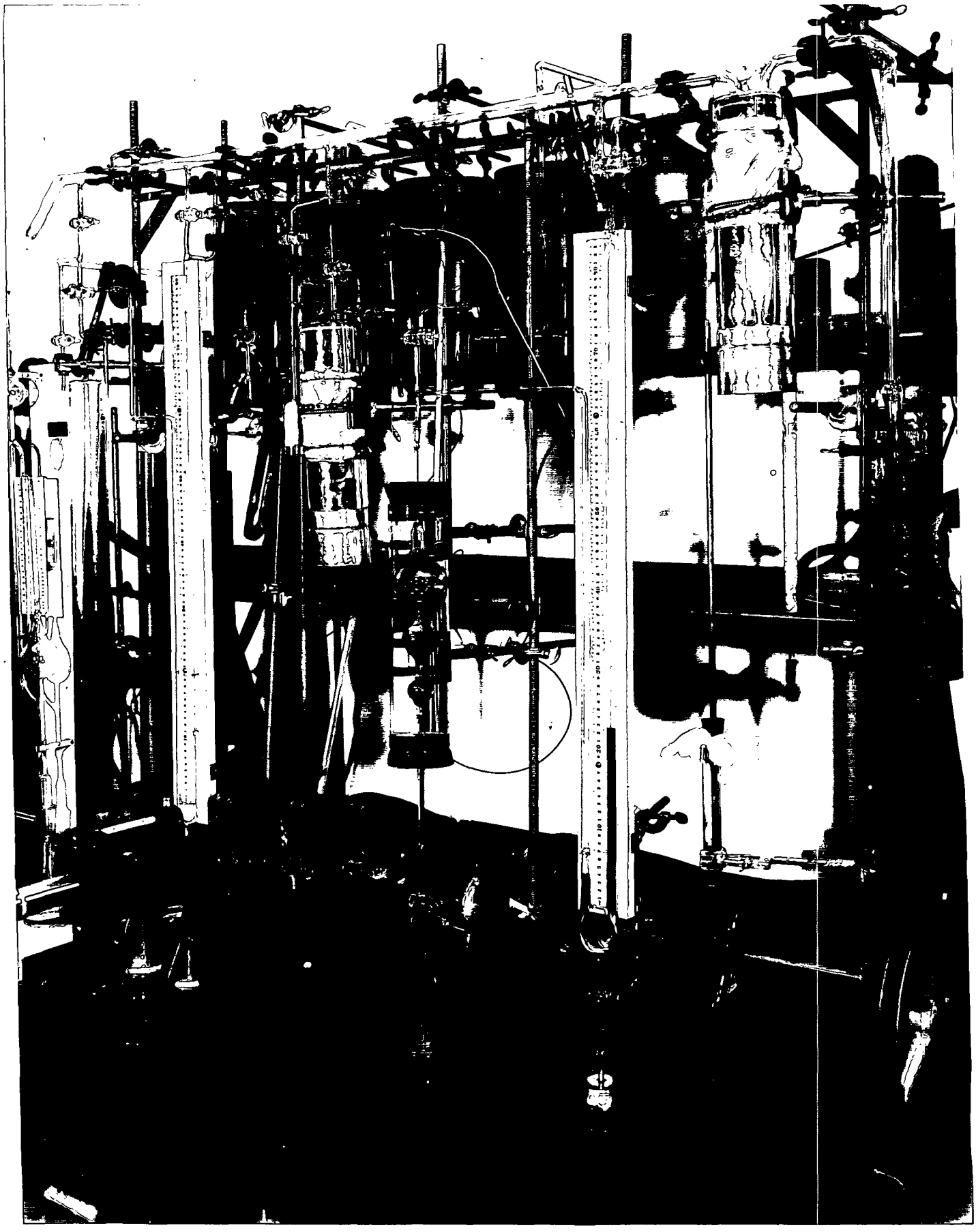


Figure 1. Photograph of Adsorption Apparatus

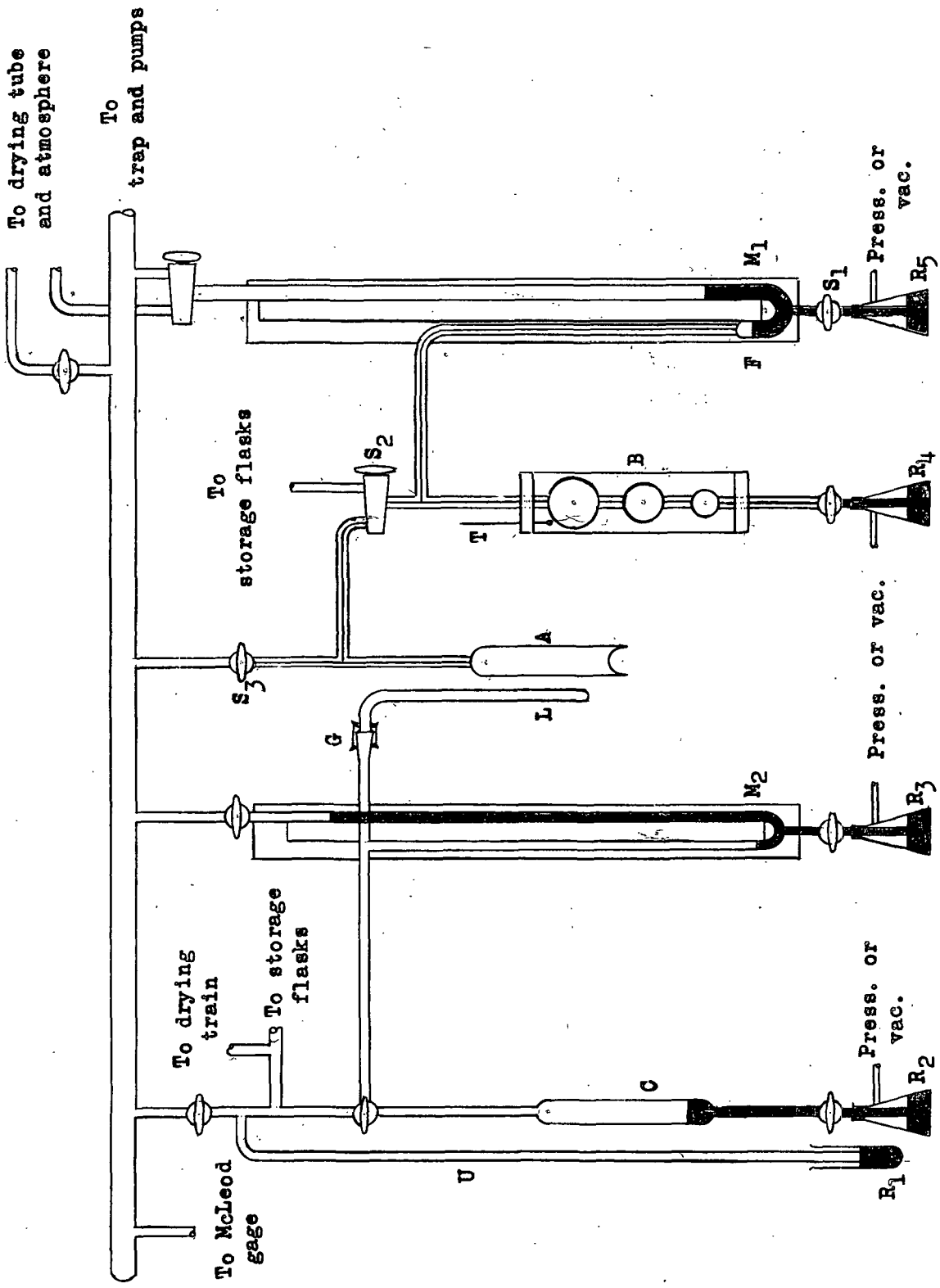


Figure 2

Apparatus for Determination of Adsorption Isotherms

manometer is 850 mm. in length, and is constructed, as is the lower portion of the left-hand leg, of a single piece of 12-mm. tubing. Mercury for M_1, and the other manometer and bulbs, is stored in the reservoirs R_1 to R_5. All but R_1 can be connected to either vacuum or approximately 10 p.s.i. pressure when necessary. The three-way stopcock S_2 permits the gas buret and the left-hand leg of the manometer to be connected either to the adsorption bulb or to the storage flasks. These flasks contain the various gases under a pressure not exceeding 900 mm. of mercury. Four flasks, each of three-liter capacity, are available for storage purposes. Individual flasks are surrounded by metal cans for protection.

The compression chamber (C) of 70-ml. capacity and the tube leading to the manometer M_2 (8-mm. tubing) are filled with the gas whose adsorption isotherm is to be determined. When the gas is compressed by filling (C) with mercury, the vapor condenses into a liquid in tube (L) which is immersed in the same bath as the adsorption bulb. The vapor pressure of the liquid is read on manometer M_2 with the aid of a meter stick. Tube (L) is connected to the apparatus through a spring-held ground-glass joint (G) which permits it to be swung out of the way when connecting or removing an adsorption bulb.

Barometric leg (U) has been included to prevent the pressure in the system from exceeding 900 mm. of mercury when the storage flasks are being filled. When filling is carried out, the various gases are passed from compressed-gas cylinders through a drying train consisting of a tube filled with Anhydrone followed by a similar tube containing alternate layers of Anhydrone and phosphoric anhydride mixed with glass wool. For all gases except n-butane, a trap immersed in a Dry Ice-alcohol bath is placed ahead of the drying train to further aid in removing moisture.

GENERAL EXPERIMENTAL PROCEDURES

PRETREATMENT OF GASES

Prior to use, the nitrogen, n-butane, carbon dioxide, and helium were thoroughly dried. The first three gases were adsorbates, whereas the helium was used to determine the volume of the adsorption bulb not filled with adsorbent (so-called "dead space"). The stated purity of these compressed gases as obtained from the suppliers is as follows: nitrogen, 99.9; n-butane, 99.0; helium, 99.8; and carbon dioxide, 99.5%.

The carbon dioxide and nitrogen were used after drying by passing through the trap and drying train previously discussed. In addition to being dried, the helium was purified by passage over evacuated activated charcoal at -78°C. After drying, it was found necessary to further purify the butane by liquefaction and evaporation, with rejection of the first third of the gas that evaporates. The resulting butane had a vapor pressure of 776 mm. of mercury at 0°C., as compared to 772 mm. given by Aston and Messerly (55) as the corresponding vapor pressure for n-butane. This indicates that the gas was relatively free of isobutane or other impurities.

CALIBRATION OF THE ADSORPTION EQUIPMENT

Since the volumetric method of isotherm determination necessitates repeated measurement of the pressure of the gas contained in a known volume, the apparatus must be initially calibrated to accurately measure this volume. If reference is made to Figure 2, it will be noted that with stopcock S_2 closed, the effective buret volume is made up of gas buret (B) down to the level of the mercury, the

capillary tubing up to S_2 and over to manometer M_1, and that volume of the left-hand leg of M_1 down to the mercury level. So that this volume is fixed, a fiducial mark (F) was placed on this leg of the manometer, and the mercury level was adjusted to this point whenever a pressure reading was taken. Prior to assembling the apparatus, the volume of each of the two lower bulbs of the gas buret was determined by weighing the quantity of mercury which each could hold. With these volumes known, it was possible to determine the total volume described above after the equipment had been assembled. To accomplish this, the mercury in manometer M_1 was drawn down into reservoir R_5 and stopcock S_1 was closed. The manometer and the buret system were evacuated, mercury was admitted to M_1, and a quantity of helium was admitted through stopcock S_2 until the mercury level was at (F). The pressure in the system was measured by reading the mercury levels to the nearest 0.1 mm. with a cathetometer. The lower bulb of the gas buret was then filled with mercury from reservoir R_4, the mercury level was returned to (F), and the pressure was again determined. Since the volume of the lower bulb was known, the desired volume of the buret system could be calculated. As a check, the second bulb of the buret was filled with mercury and the procedure was repeated. The total volume of the buret system determined in this way was 150.4 ml.

MEASUREMENT OF ADSORPTION ISOTHERMS

The procedure involved in obtaining isotherm data is relatively simple and is essentially the same for any gas. In the following description of this procedure, however, it will be assumed that nitrogen is the adsorbate. Reference should be made to Figure 2 in following the discussion.

After adsorption bulb (A) had been filled with the sample and had been sealed

to the apparatus, S_3 and the other connections to the vacuum header were opened. Evacuation, first with only the rotary oil pump and finally with both this and the diffusion pump, was carried out until the pressure read on the McLeod gage was approximately 10^{-4} mm. All open stopcocks were then closed, and mercury was run up into manometers M_1 and M_2. Liquid nitrogen, contained in a wide-mouth vacuum flask, was placed around the adsorption bulb (A) and the tube (L). Nitrogen from a storage flask was admitted to the compression bulb (C), tube (L), and the left-hand side of manometer M_2. As the compression bulb was gradually filled with mercury from reservoir R_2, the nitrogen was liquefied in the end of (L) and its vapor pressure was measured to the nearest 0.5 mm.

Next, helium was admitted through stopcock S_2 until the pressure in the gas buret was 200 to 300 mm. As was done before every pressure measurement, the left-hand leg of manometer M_1 was adjusted to mark (F) and the pressure read to the nearest 0.1 mm. with a cathetometer. The temperature of the water jacket was also read to the nearest 0.1°C. with thermometer (T) at this and all subsequent pressure measurements. By turning stopcock S_2, the helium was allowed to expand into the adsorption bulb. The mercury levels in the manometer changed, and when equilibrium was reached, the pressure was again determined. Since at temperatures of -196°C. and above, helium is not appreciably adsorbed by the sample but merely fills the space around it, these measurements permitted the calculation of the "dead space". For an excellent description of the calculations involved in computing the "dead space" and adsorbed gas volumes, reference should be made to Bugge and Kerlogue (56). Duplicate "dead space" determinations commonly checked to better that 0.3 ml. (S.T.P.).

The low-temperature bath was removed, the mercury in M_1 was pulled down into the reservoir, and the entire right side of the apparatus was evacuated to 10^{-4} mm. Stopcocks S_2 and S_3 were then closed, and the adsorption bulb and tube (L) were immersed in liquid nitrogen. Mercury was allowed to rise in the manometer, a small quantity of nitrogen was admitted through S_2, and the pressure was read. The gas was allowed to expand into the adsorption bulb, and when equilibrium was reached, the pressure was again determined. Stopcock S_2 was then adjusted to permit entry of an additional small amount of nitrogen, and the above procedure was repeated until a sufficient number of points on the adsorption isotherm were obtained.

When nitrogen is the adsorbate, the volume of gas (S.T.P.) adsorbed at each equilibrium pressure is given by the equation

$$\underline{v} = \underline{V}_t - \underline{V}_h \, (1 + \alpha \, \underline{p} \, / \, 760) - \underline{V}_b , \qquad (43)$$

where $\underline{v}$ is the volume of gas adsorbed, $\underline{V}_t$ is the total volume of adsorbate that is initially in the buret system, $\underline{V}_h$ is the volume of the adsorbate required to fill the "dead space" to pressure $\underline{p}$ of the experiment, α is the correction factor required to take into account the gas imperfection of the nitrogen at the low temperature being used, and $\underline{V}_b$ is the volume of the gas remaining in the buret when adsorption equilibrium has been reached. Equation (43) must be modified when the adsorbate is n-butane or carbon dioxide since, in addition to $\underline{V}_h$, both $\underline{V}_t$ and $\underline{V}_b$ must be corrected for deviation of these gases from the perfect gas laws at room temperature.

THE ADSORPTION OF NITROGEN, n-BUTANE, AND CARBON DIOXIDE BY WOOD AND ITS COMPONENTS

An investigation was undertaken of the nature of the low-temperature adsorption of nitrogen, n-butane, and carbon dioxide on wood and its major components. The adsorption of gas, of course, could not be determined separately on these components *in situ*. Therefore, the main portion of the work was concerned with gas adsorption on extracted sprucewood, sprucewood from which mainly only lignin had been removed by treatment with acidified sodium chlorite solution, and this chlorite holocellulose after further treatment with alkali to remove hemicelluloses.

EXPERIMENTAL PROCEDURES

PREPARATION OF ADSORBENTS

The starting material employed for preparation of all materials studied in the course of the experimental work was five peeled sticks of Canadian-grown black spruce (*Picea mariana*) which had an average diameter of 6 inches and an average age of 75 years.

A portion of wood from each stick was reduced to sawdust, air dried, and ground in a Wiley mill. Only the 40- to 60-mesh fraction was employed. The wood meal was extracted for three days in a Soxhlet extractor with a mixture of 33% ethanol and 67% benzene. After extracting and air drying to remove most of the organic solvents, the wood meal was stirred for two hours in a large quantity of distilled water at 95°C. This step removed the water-soluble material and also the organic solvents remaining in the wood from the previous operation. These treatments removed 4.6% extractives, based on the original ovendry wood. The extracted wood was analyzed for apparent pentosans by the bromide-bromate technique (Institute Tentative Method 32a) and for Klason lignin by Institute Method 13. The results of

these analyses are given in Table II.

TABLE II

ANALYSIS OF SAMPLES

	Extracted Sprucewood	Chlorite Holocellulose	5% KOH-extracted Chlorite Holocellulose
Apparent pentosans, %	9.7	10.8	5.0
Klason lignin, %	27.9	4.2	1.4
Alpha-cellulose, %	50.4[a]	61.8	84.4

[a] Calculated from yield data and the alpha-cellulose content of the chlorite holocellulose

Approximately 900 g. of the air-dried extracted wood meal was subjected to sodium chlorite oxidation employing large-scale equipment similar to that described by Barton (57) but following the procedure given in Institute Method 28 as closely as possible. As a final step, the holocellulose was not treated with acetone, but was air-dried after a thorough washing with ice water. The yield of lignin-free chlorite holocellulose based on the extracted wood was 78%. In Table II are given the results of a determination of the pentosan content (Institute Method 424a), the Klason lignin content (Institute Method 428), and alpha-cellulose (Institute Method 421a) made on the chlorite holocellulose.

A portion of the chlorite holocellulose was extracted with 5% potassium hydroxide under nitrogen according to the method of Wise, Murphy, and D'Addieco (58). A lignin-free product yield method of 73% based on the holocellulose, and 58% based on the extracted wood, was obtained. Analyses similar to those run on the holocellulose were carried out, and these results are also reported in Table II.

Approximately 110 g. (enough to fill three adsorption bulbs) of the extracted sprucewood, the chlorite holocellulose, and the KOH-extracted chlorite holocellulose were ground in a Wiley mill so that the material would pass a 120-mesh U.S. Standard screen. The ground samples were dried in an evacuated desiccator over phosphoric anhydride for five days. The moisture content of the specimens was reduced to 0.4 to 0.8% by this treatment.

Nine adsorption bulbs were constructed by sealing about 6 inches of 1-mm. capillary tubing to the base of a 28-mm. test tube after removal of the flared rim. Approximately 2 inches of the bottom of a 25-mm. test tube were removed to be used as the bottom of the adsorption bulb. The complete assembly was weighed before and after filling to determine the weight of sample in each bulb. Three of these bulbs were filled with dry, thoroughly mixed wood meal, and the 25-mm. test tube bottom pressed in until the cut rims were flush. The two tubes were then fused together to complete the operation. In a similar fashion, three bulbs were filled with dried chlorite holocellulose and three with dried, alkali-extracted chlorite holocellulose. Each bulb contained approximately 30 g. of material.

COMPOSITION AND TEMPERATURE OF THE COLD BATHS

The main portion of the adsorption studies with nitrogen and n-butane were carried out very close to the respective liquefaction temperatures of the gases. When the adsorbate was carbon dioxide, a temperature near the normal sublimation temperature was used. In order to employ the various methods of estimating surface area, the saturated vapor pressure of the adsorbate at the temperature of the respective cold bath is required. In each instance, this was obtained by determining

the saturated vapor pressure of the adsorbate with the vapor pressure portion of the equipment.

In addition, it was necessary to select and use other constant-temperature baths, which differed by 10 to 25°C. from those primarily employed to obtain the data necessary for the computation of the differential heat of adsorption by the Clausius-Clapeyron equation. Accurate determination of the temperatures of all baths is essential if reliable values of the differential heats of adsorption are to result. Table III gives the composition and the average temperature of the various constant-temperature baths.

TABLE III

COMPOSITION AND TEMPERATURE OF COLD BATHS

Adsorbate	Composition	Normally Observed Temperature, °C.
Nitrogen	liquid nitrogen	-195.7
	liquid oxygen	-182.9
n-Butane	cracked ice	0.0
	sodium chloride-ice eutectic	-21.2
Carbon dioxide	Dry Ice-ether	-78.6
	liquid ethane	-89.3

The liquid nitrogen and liquid oxygen, required when nitrogen was the adsorbate, were obtained from a producer of compressed gases. Nitrogen and oxygen were employed in the vapor pressure system when liquid nitrogen and liquid oxygen baths, respectively, were being used. The bath temperature in each case was determined from the saturated vapor pressure by means of equations given by Bugge and Kerlogue (56).

The temperature of the sodium chloride-ice bath employed in the studies with n-butane was checked by the measurement of the saturation vapor pressure of n-butane and the application of an equation given by Aston and Messerly (55).

When the adsorbate was carbon dioxide and Dry Ice-alcohol and Dry Ice-acetone mixtures were used as constant-temperature baths, it was found that solid carbon dioxide would not form in a tube immersed in the bath at pressures under 860 mm. of mercury (the practical limit of the equipment). However, when ethyl ether and Dry Ice were used as the cold bath, compression to approximately 800 mm. resulted in the appearance of solid carbon dioxide crystals in the tube. Apparently, the Dry Ice-ether mixture is just sufficiently colder than the baths obtained with acetone or ethanol, to permit carbon dioxide to be solidified below 860 mm.

The equilibrium vapor pressure of the carbon dioxide system, however, was not as quickly and directly reached as had occurred for nitrogen and n-butane. Rather, after the pressure was increased to initiate the formation of a feathery precipitate of solid carbon dioxide in the end of the condensation tube, the pressure of the gas in the system fell rapidly. This decrease in pressure generally continued until 600 to 675 mm. were reached. The pressure then began a slow steady rise to a relatively constant value in the range of 740 to 760 mm. Due to this somewhat peculiar behavior of the saturated carbon dioxide before coming to equilibrium pressure, it was thought desirable to check the bath temperature measured in this manner. This was done first by measuring the vapor pressure of anhydrous liquid ammonia at the temperature of the bath and employing vapor pressure-temperature data given by Perry (59). A chromel-alumel thermocouple was also used to estimate the bath temperature. The thermocouple was calibrated with solid carbon dioxide and a cracked ice reference bath. Measurement of the barometric pressure

permitted the temperature of the Dry Ice calibration bath to be accurately determined (60). Once calibrated, temperatures were determined using voltage-temperature tables (60) for chromel-alumel thermocouples. Temperatures corresponding (61) to measured values of the saturated vapor pressure of carbon dioxide were also obtained. The temperature of the ether-Dry Ice bath as measured by these three methods over a period of time is given in Table IV.

TABLE IV

TEMPERATURE OF ETHER-DRY ICE BATH

Method of Measurement	Temperature Range of Readings	Average Temperature
Carbon dioxide vapor pressure	-78.5 to -78.9°C.	-78.7°C.
Anhydrous ammonia vapor pressure	-78.5 to -78.7	-78.6
Chromel-alumel thermocouple	-78.0 to -78.8	-78.4

It is apparent from Table IV that the bath temperature as determined using the thermocouple, varied more and averaged somewhat less than that for the ammonia or carbon dioxide. In all instances, however, the averages are quite close together. Since the bath temperature as measured by carbon dioxide vapor pressure, was substantiated so well by the values obtained using the ammonia or the thermocouple, and also since the use of carbon dioxide made a direct reading of the saturated vapor pressure possible, this method was employed for the carbon dioxide runs.

Liquid ethane for the other cold bath employed with carbon dioxide was prepared by slowly permitting tank ethane of 99.8% purity to condense in an evacuated Kjeldahl flask cooled in a slush of absolute ethyl alcohol and liquid nitrogen.

The temperature of the liquid ethane bath was measured using ethane in the vapor pressure system. In this way, the average temperature as determined (61) from the saturated vapor pressure was -89.3°C.

EXPERIMENTAL RESULTS AND DISCUSSION

DEVIATION OF n-BUTANE FROM THE PERFECT GAS LAWS

When determining the amount of adsorbed gas using Equation (43), it is necessary to correct the volume of gas in the "dead space" to account for the gas imperfection at the low temperatures being used. For n-butane and carbon dioxide, similar corrections must also be applied to volume measurements made at room temperature. Values of the correction factor for the more common gases at several temperatures have been calculated by Emmett and Brumauer (3) from various literature data. For n-butane (at 760 mm.) this correction was given as 10.8% at 0°C. and 3.2% at 25°C., and it is stated by Emmett and Brunauer that they computed these values from work on n-butane reported by Dana, Jenkins, Burdick, and Timm (62). These correction factors were initially used in determining the first n-butane isotherm. It was noted, however, on desorption, that the points fell increasingly above the adsorption curve as the pressure was decreased in a manner entirely different from that observed for a hysteresis loop. It was speculated that this might be due to an accumulating error in computing the volume of gas in the gas buret at each pressure. Therefore, an independent determination of the correction factors was made for n-butane at room temperature (23°C.), 0°C., and also at -21.2°C. for use in the adsorption studies made at that temperature.

In place of an adsorption bulb containing adsorbent, an empty bulb was sealed onto the equipment. With the bulb at 23.0 ± 0.1°C., the volume of the bulb was

determined using helium, which at this temperature acts as a perfect gas. Pressure readings were made of the n-butane before and after it was allowed to expand into the known volume of the evacuated bulb. Calculations were then carried out to determine the best value of the correction factor α to explain the experimentally observed results. As shown in Table V, this is 2.7%. When this value was employed to correct the n-butane for deviations at room temperature, the desorption points in the work previously discussed generally fell on the adsorption curve.

TABLE V

CORRECTION FACTORS FOR THE DEVIATION OF n-BUTANE FROM THE PERFECT GAS LAWS

	23.0°C.	0°C.	-21.2°C.
Average value from pressure-volume measurements, %	2.7	5.0	6.0
Determined from the data of Dana, et al., %			
By Emmett and Brunauer	3.8[a]	10.8	--
By the author	3.4	5.8	--
Calculated using the Berthelot equation, %	3.0	3.9	5.1

[a] Estimated from the value given for 25°C.

Using the correction factor of 2.7% at room temperature, factors were also determined at various pressures with the bulb at 0 and -21.2°C. It was found that the necessary correction tended to decrease somewhat as the pressure increased but became relatively constant at higher pressures. From these data, average values of the correction factor were found to be 5.0% at 0°C. and 6.0% at -21.2°C. These values are given in Table V, together with values at 23 and 0°C. calculated both by Emmett and Brunauer and by the author from the data of Dana, Jenkins, Burdick, and Timm (62). Similar correction factors at all three temperatures determined using the Bethelot equation of state are also included. The correction factors experimentally measured in the present work are lower than those reported by Emmett and Brunauer especially at 0°C. Also, in each instance, the values calculated by the Berthelot equation and from the work of Dana, Jenkins, Burdick, and Timm are lower than the reported correction factors but are in fair agreement with the

measured values. Therefore, the correction factors determined in the present study were employed for all adsorption investigations with n-butane.

ADSORPTION STUDIES ON SPRUCEWOOD, CHLORITE HOLOCELLULOSE, AND KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Isotherms were determined for the adsorption of n-butane (at 0 and -21.2°C.) and nitrogen (at -195.7 and -182.9°C.) on finely ground samples of extracted sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose. These data, which are given in the Appendix in Tables A to C, are plotted in Figures 3 to 5. In determining each point on the isotherms, readings of pressure were taken every five minutes with the cathetometer until a change of less than 0.1 mm. of mercury was recorded. For nitrogen and n-butane, equilibrium was reached in 10 to 20 minutes.

Adsorption of Nitrogen

The adsorption of nitrogen at -195.7°C. gave typical S-shaped isotherms so commonly found with this adsorbate at liquid nitrogen temperatures. For measurements at -182.9°C., the curves showed no upward swing. The latter isotherms are probably S-shaped, but because of the limitations of the apparatus, it was not possible to investigate the higher relative pressures where the rapid increase in adsorption would occur.

On each of the three different adsorbents, desorption points were determined after the initial nitrogen adsorption (at -195.7°C.) was measured. The adsorbent was then evacuated, and points on a second adsorption isotherm were determined. It was found, in all instances, that the second isotherm was almost exactly the same

Figure 3

Adsorption of Nitrogen and n-Butane

on Sprucewood

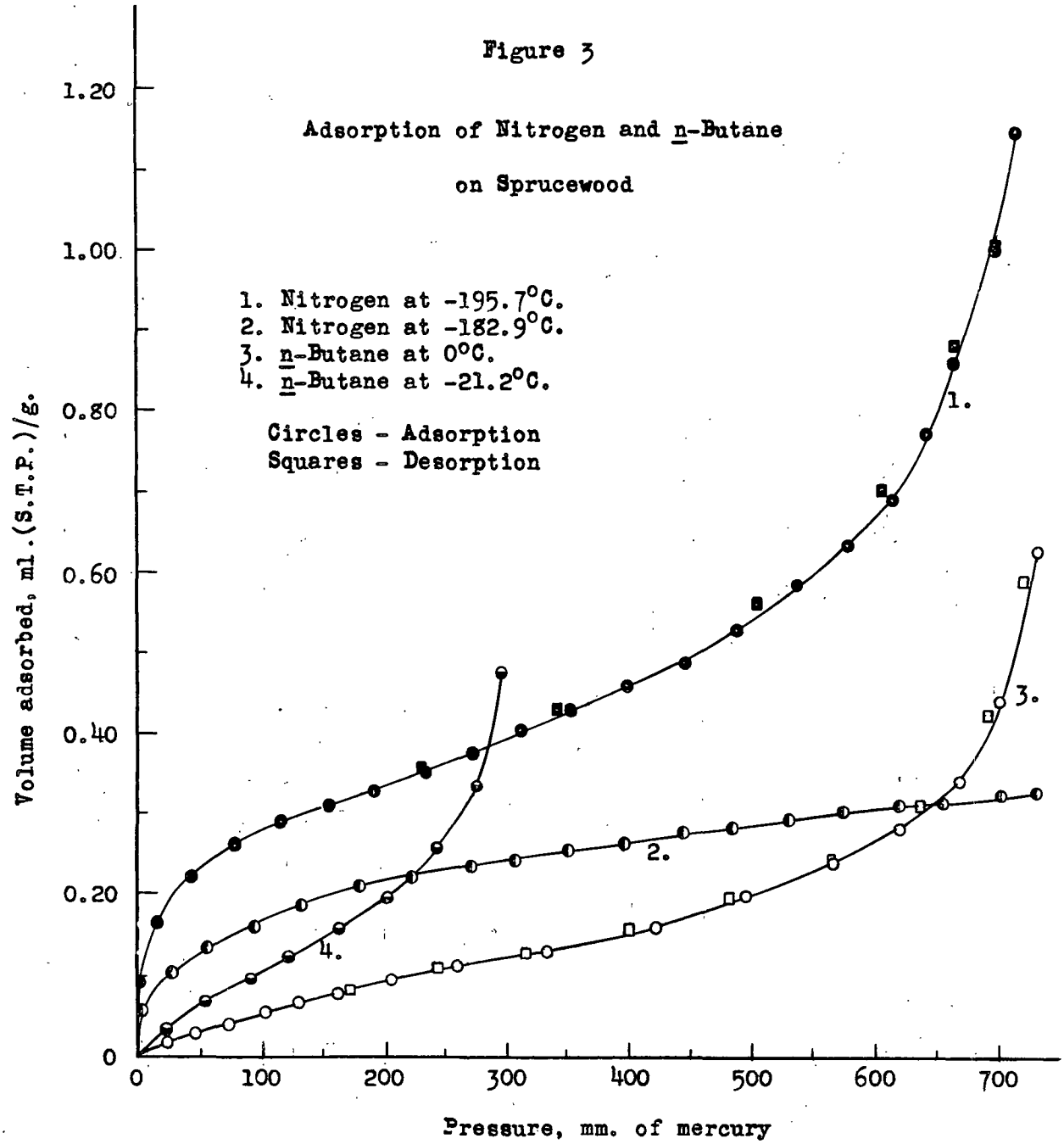


Figure 4

Adsorption of Nitrogen and n-Butane

on Chlorite Holocellulose

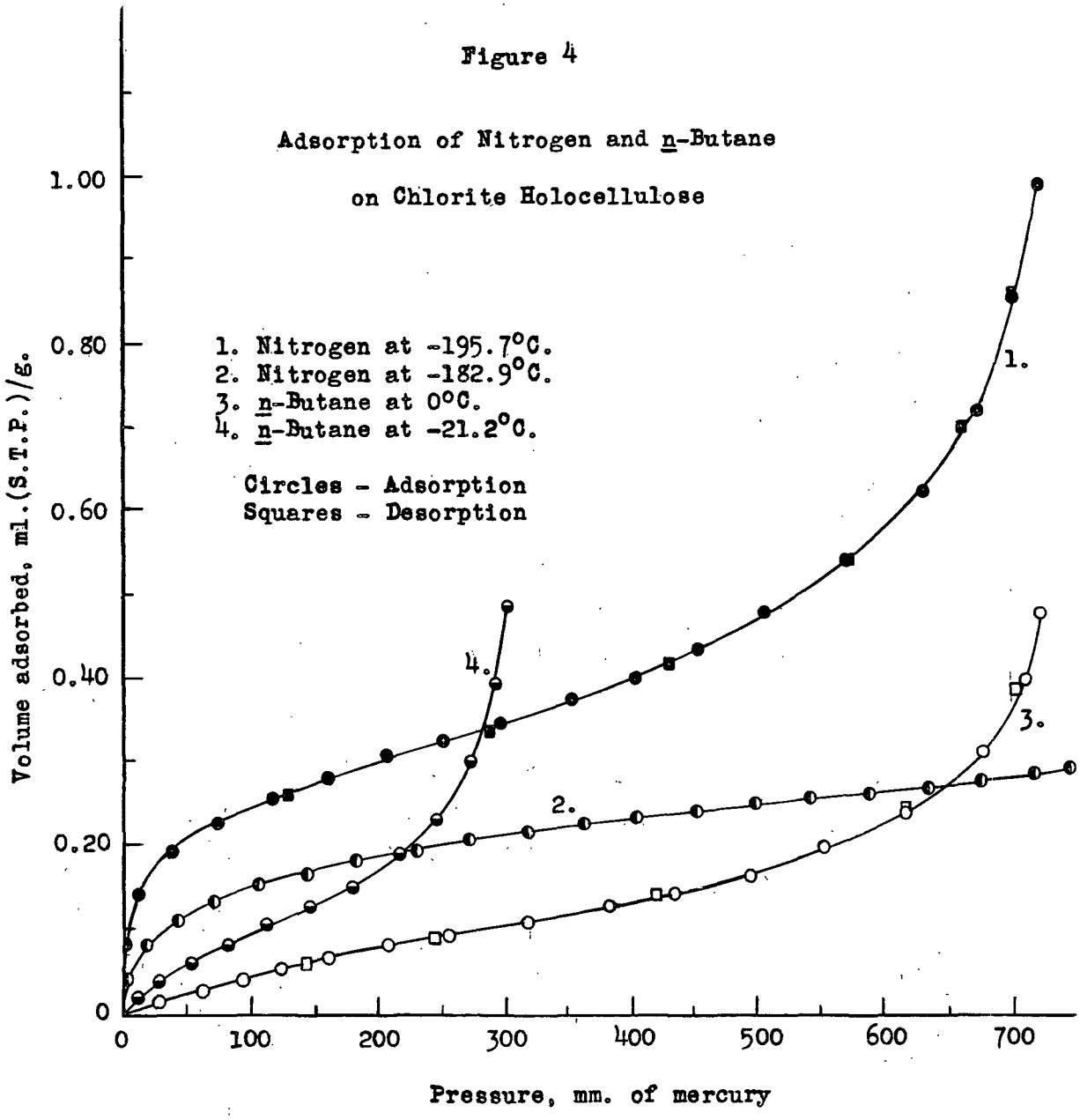
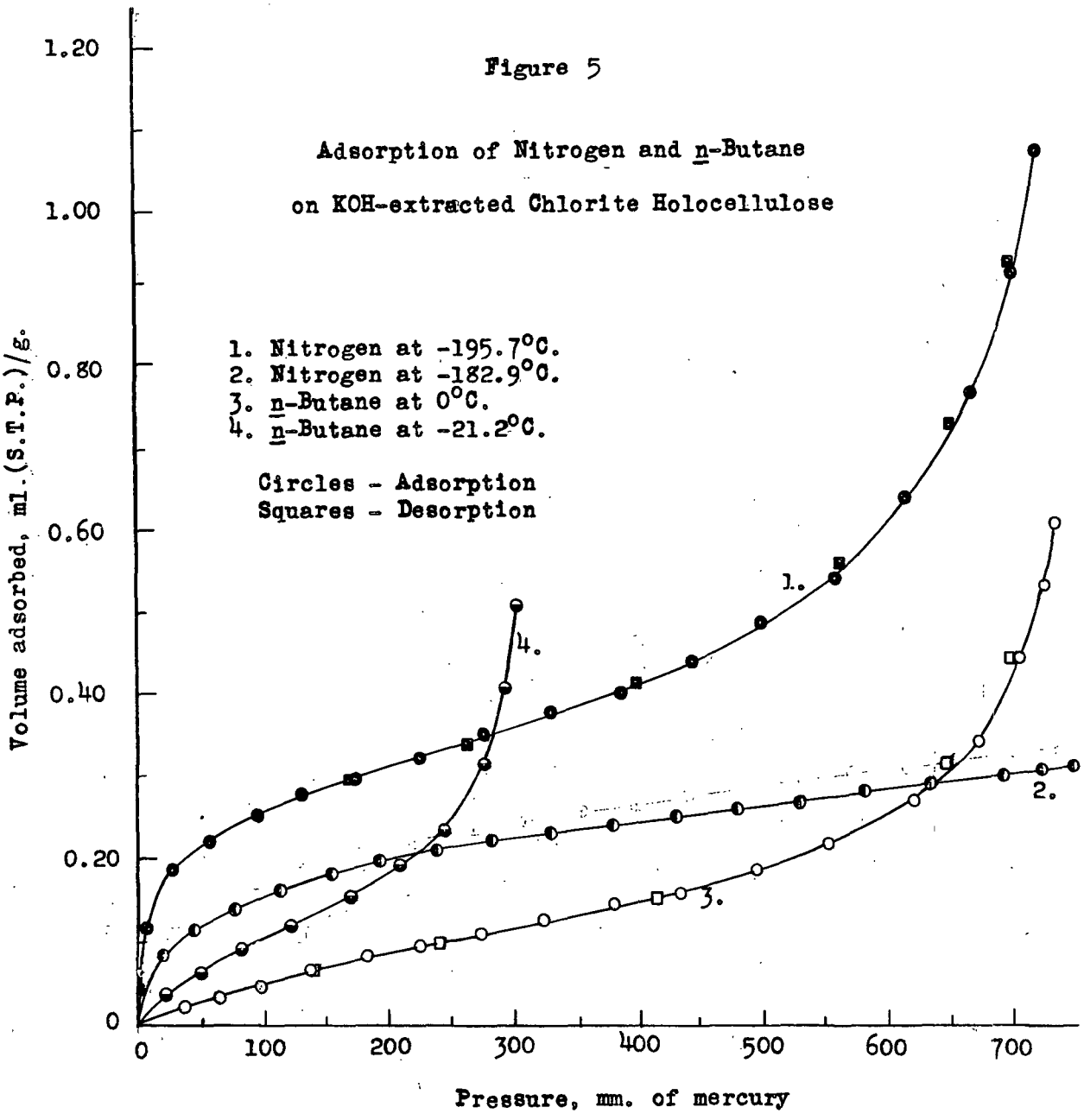


Figure 5

Adsorption of Nitrogen and n-Butane

on KOH-extracted Chlorite Holocellulose



as the first. This can be taken to indicate that the nitrogen was in no way combining with the adsorbents and that all of the adsorbed nitrogen was removed on evacuation. The desorption points fell generally on the adsorption curve except at the higher pressures where they were occasionally slightly above it. This latter situation is most apparent for the desorption curve of nitrogen on sprucewood (Figure 3 - curve 1) where a faint hysteresis loop is noted. This would tend to indicate that the sprucewood had more accessible pores than the other adsorbents. However, none of these materials could be strictly termed porous.

The points on the B.E.T. plots (see Table D in the Appendix) of the nitrogen adsorption data given in Figure 6 generally follow a straight line until a relative pressure of 0.30 is reached. From the slope and intercept of these lines, v_m, the monolayer volume adsorbed on each of the materials was determined. Throughout the experimental work a "method of averages" discussed by Davis (63) was used to eliminate the factor of personal judgement in determining the slope and intercept of all straight-line plots. This technique involves a division of the data into two adjacent groups and substituting the experimental values into an empirical equation. The equations are added and the two resulting simultaneous equations are solved for the slope and, in the case of B.E.T. plots, the intercept at $p/p_o = 0$. Since 16.2 sq. A. has been used most frequently by other workers as the cross-sectional area of an adsorbed nitrogen molecule, this was the value initially employed. The calculated areas are given in Table VI.

Figure 6

B.E.T. Plot of Nitrogen Adsorption at -195.7°C.

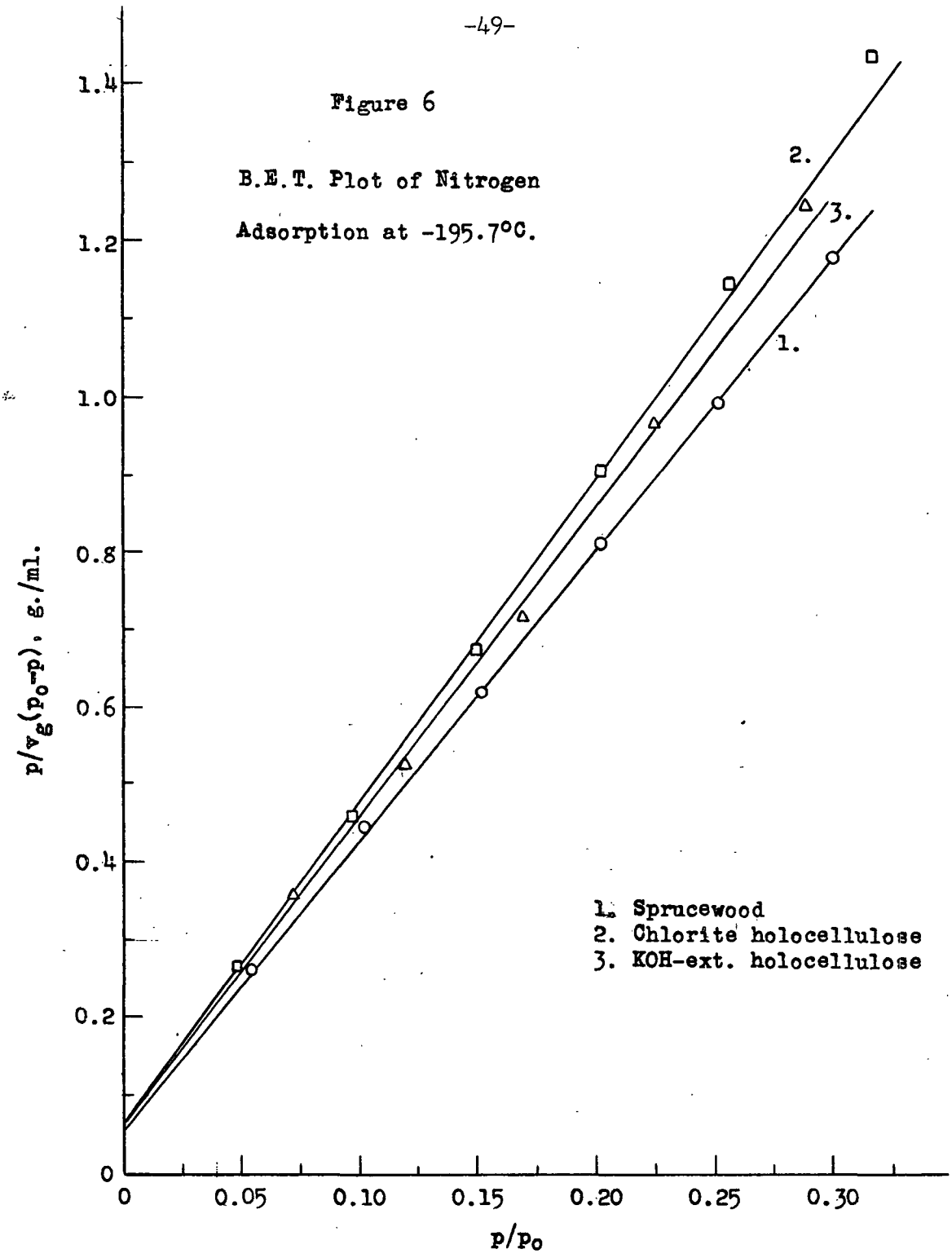


TABLE VI

SPECIFIC SURFACE AREAS DETERMINED FORM NITROGEN ADSORPTION MEASUREMENTS AT -195.7°C.

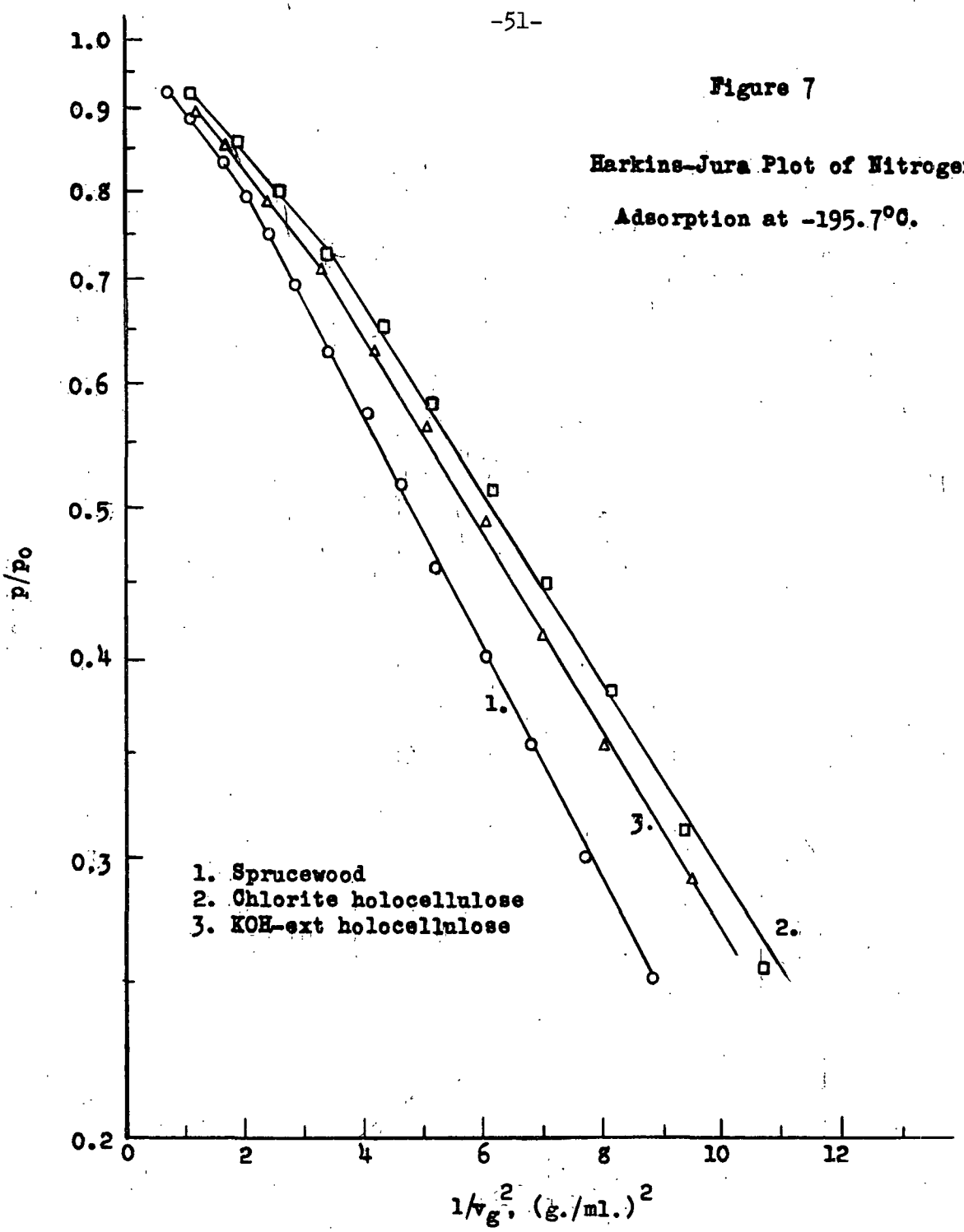
	Area, sq. m. per gram		
	Extracted Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
B.E.T. method			
Mol. area, 16.2 sq. A.	1.14	1.04	1.06
Mol. area, 15.7 sq. A.	1.11	1.01	1.03
Harkins-Jura method	1.11	1.01	1.02
Fu-Bartell method	1.06	0.80	0.81

In Figure 7, the nitrogen adsorption data are plotted according to the method developed by Harkins and Jura (18). These values are also given in Table E in the Appendix. As is commonly observed, the points obtained can be approximated by two intersecting straight lines. It is the slope occurring at the lower pressure that is employed to compute the surface area. The constant k in the Harkins-Jura equation for nitrogen at -195.7°C. is 4.06 and this multiplied by the square root of the various slopes gives the areas listed in Table VI.

It is seen that although the difference is small, the areas determined by the Harkins-Jura method are in each case less than those determined by the B.E.T. method if 16.2 sq. A. is used for the molecular area of nitrogen. When instead (see Table VI) a value of 15.7 sq. A. is employed for the molecular area, the check is excellent. This would indicate that Livingston (64) may be justified in stating that the "best" value to use for the cross-sectional area of an adsorbed nitrogen

Figure 7

Harkins-Jura Plot of Nitrogen Adsorption at -195.7°C.



molecule is 15.4 sq. A. instead of the more commonly employed value of 16.2 sq. A. obtained by Emmett and Brunauer (3) from a consideration of the density of liquid nitrogen. The value of 16.2 sq. A. was given apparent verification by Harkins and Jura (18) when it was found that this figure gave an excellent check for the areas of crystalline solids as computed by their method and the B.E.T. equation. It should be pointed out, however, that for over 100 samples of various materials investigated in the same way by Harkins and Jura, the value giving the "best fit" between the two methods was 15.4 sq. A. Whereas this may indicate that 16.2 sq. A. is somewhat high, there is, of course, no assurance that the Harkins-Jura method gives the more accurate area values. A nitrogen molecule area of 15.7 sq. A. used with the B.E.T. equation may give the best agreement with the Harkins-Jura area for the present data, but the use of 16.2 sq. A. may very well result in an area closer to the actual specific surface area of the samples.

Figure 8 gives a plot of the type used by Fu and Bartell (27) to obtain the area of porous solids. Numerical values are given in Table F in the Appendix. The computation of the change in total free surface energy (total free surface energy = free surface energy times area) required for this plot will be subsequently discussed. For calculation of the area from Equation (30), a value of 8.85 dynes per cm. (61) was used as the surface tension of liquid nitrogen at -195.7°C. From Table VI, it is seen that although the area for the very slightly porous sprucewood is comparable to that obtained by the B.E.T. and Harkins-Jura methods, areas for the other adsorbents are substantially lower. These results are in agreement with those of Fu and Bartell who found a good check between

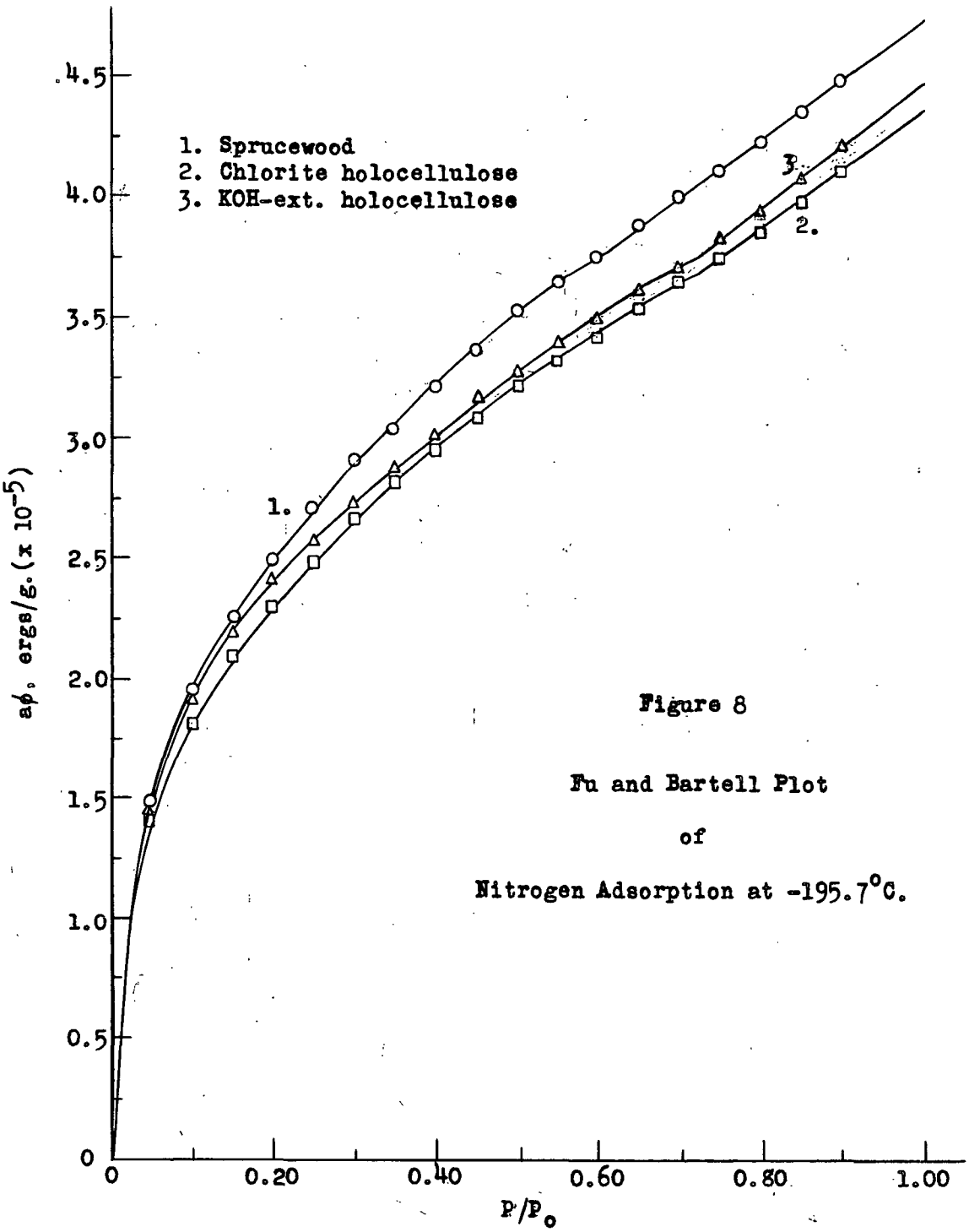


Figure 8

Fu and Bartell Plot

of

Nitrogen Adsorption at -195.7°C.

their method and the B.E.T. method for very porous and slightly porous samples of benzene-dried cotton, but that their method gave a considerably lower area for nonporous water-dried linters.

Adsorption of n-Butane

The results of the studies carried out using n-butane at 0°C. are similar to those just discussed for nitrogen. Reference to curve 3 in each of Figures 3 to 5 indicates that the desorption points are either on or, at the higher pressures, slightly above the adsorption curve. Although less than noted for nitrogen, the isotherm for the sprucewood shows slightly greater hysteresis than for the other two adsorbents. When readsorption curves were run after the samples were evacuated, the initial curves were duplicated.

Figure 9 gives a plot of the calculated values (see Table G in the Appendix) of the left-hand side of the B.E.T. equation against the relative pressure p/p_o for n-butane adsorption at 0°C. The points in this plot are somewhat more scattered than a similar plot for nitrogen and, in addition, start to show marked deviation at fairly low relative pressures. The first B.E.T. area values given in Table VII assume that the molecular area for n-butane is 32.1 sq. A. This is the value computed by Emmett and Brunauer (3) employing the density of liquefied n-butane.

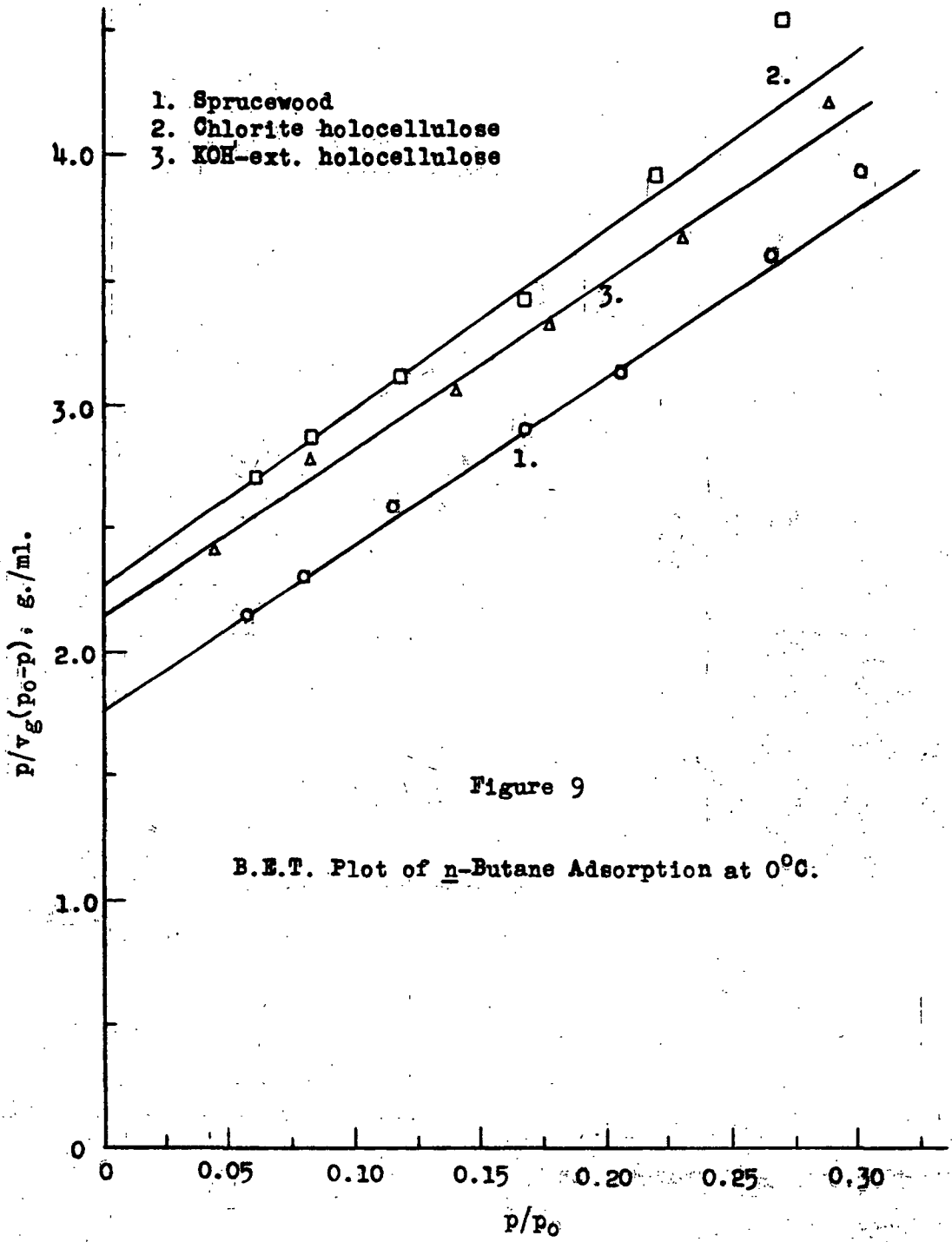


Figure 9

B.E.T. Plot of n-Butane Adsorption at 0°C.

TABLE VII

SPECIFIC SURFACE AREAS DETERMINED FROM n-BUTANE ADSORPTION MEASUREMENTS AT 0°C.

	Area, sq. m. per gram		
	Extracted Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
B.E.T. method			
Mol. area, 32.1 sq. A.	1.03	0.90	0.98
Mol. area. 35.4 sq. A.	1.14	1.00	1.08
Harkins-Jura method	1.01	0.89	1.00
Fu-Bartell method	0.79	--	--

Harkins-Jura plots (see Table H in Appendix) of the n-butane adsorption data are given in Figure 10. These differ somewhat in appearance from the similar nitrogen plots and show a strong curvature as the lower relative pressures are approached. For a k value of 13.6, the areas calculated from the slopes of these plots are given in Table VII.

Figure 11 gives a Fu-Bartell plot of the change in the total surface energy as the adsorption of n-butane proceeds. Values for this plot are listed in Table I in the Appendix. A "break" in these curves was apparent only when adsorption took place on sprucewood, limiting a computation of area to this material. A surface tension value of 15.7 dynes per cm. (65) for n-butane at 0°C. was used, and the result is given in Table VII.

When 32.1 sq. A. is taken as the molecular cross-sectional area of n-butane, the B.E.T. areas for the adsorbents compare fairly well with the areas computed by the Harkins-Jura method. These B.E.T. areas of each material computed from

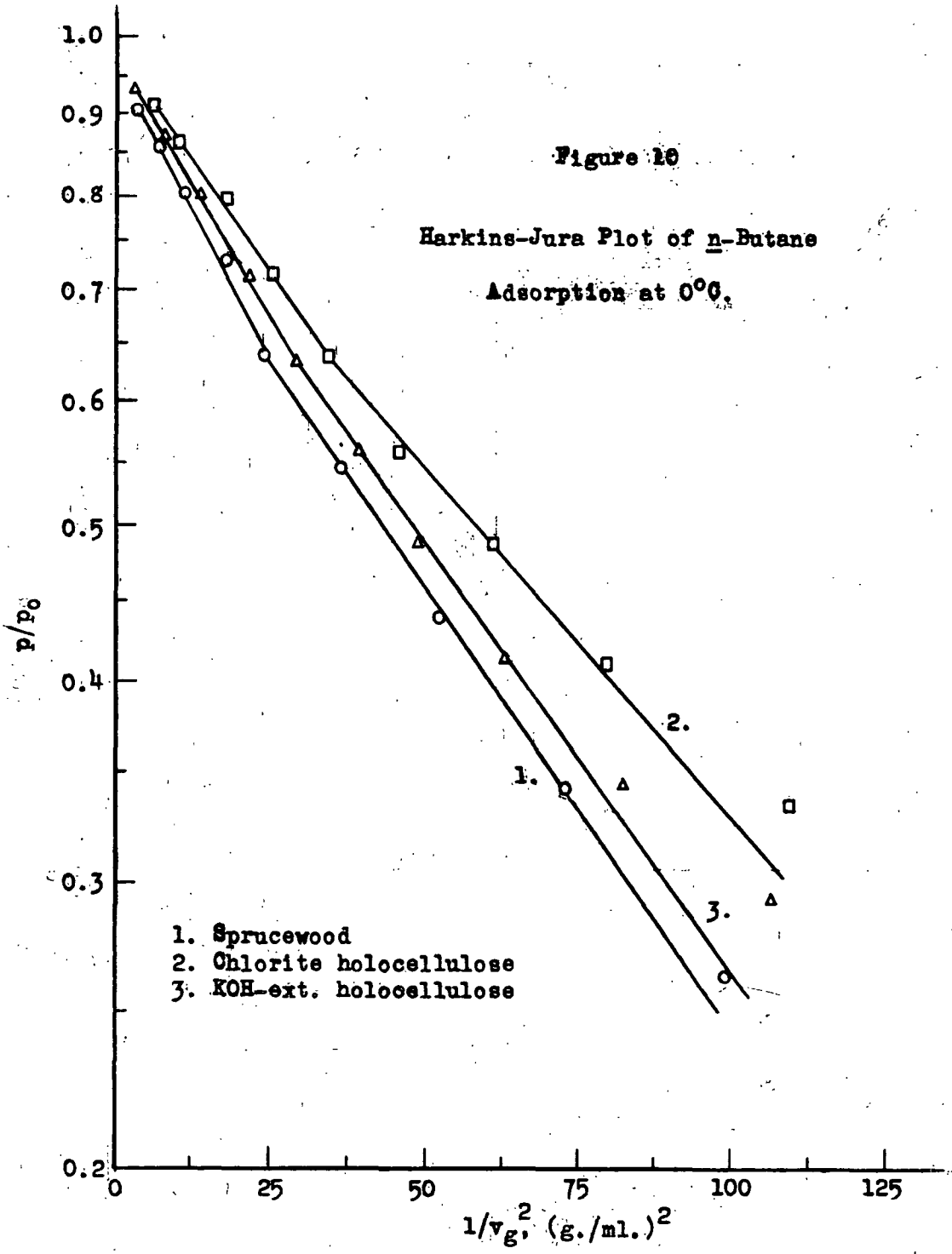


Figure 10

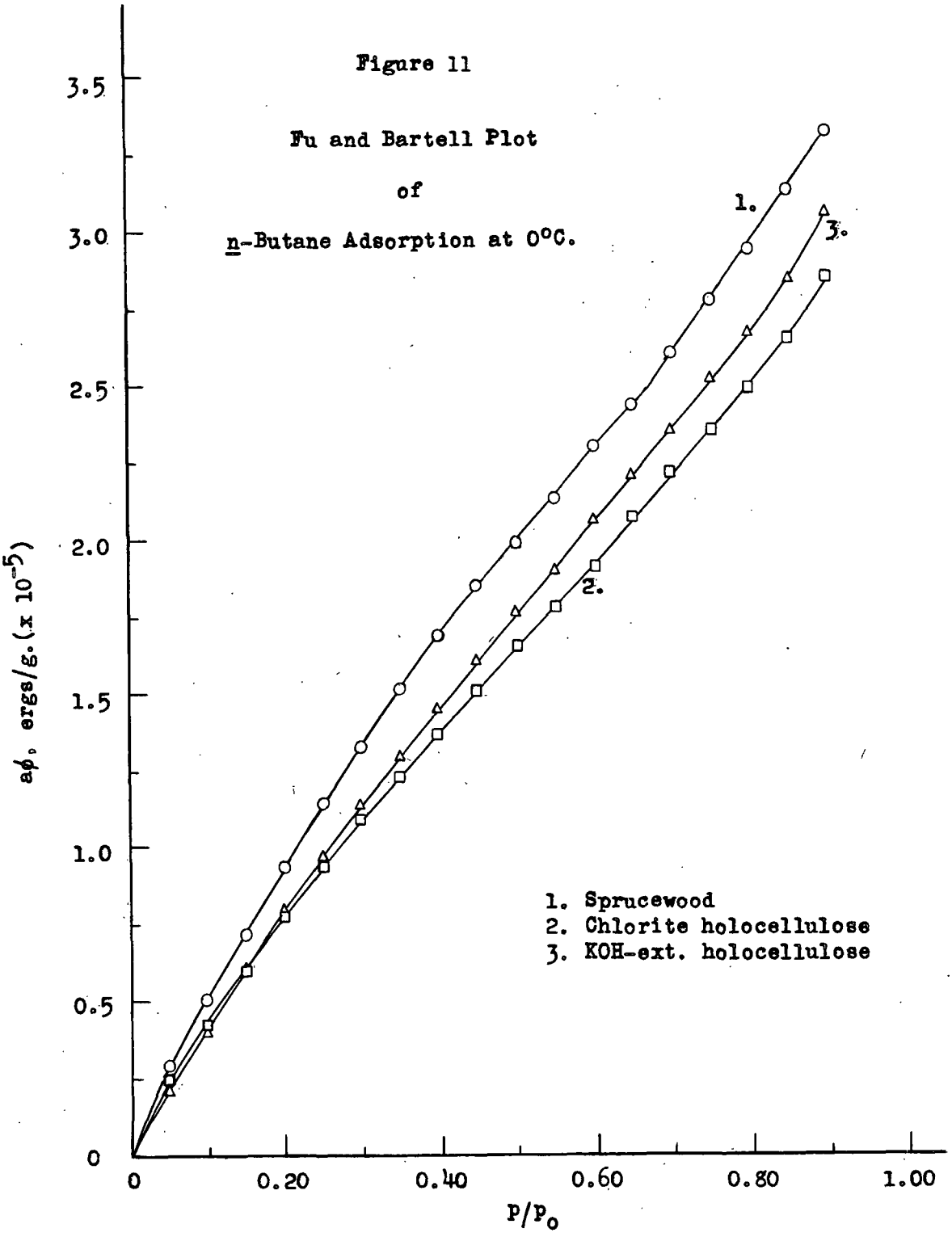
Harkins-Jura Plot of n-Butane Adsorption at 0°C.

Figure 11

Fu and Bartell Plot

of

n-Butane Adsorption at 0°C.



butane adsorption data are considerably lower than the areas of the same adsorbents determined by nitrogen adsorption. However, a comparison of Tables VI and VII shows that when an area of 35.4 sq. A. is taken for an n-butane molecule, the resulting specific surface is fairly close to the corresponding B.E.T. nitrogen area (molecular area - 16.2 sq. A.).

The proper area to assign to adsorbed butane molecules has been the source of controversy for a number of years. Harkins and Jura (18) found it necessary to use 56.6 sq. A. to obtain an area for titanium dioxide that checked with the area determined by their method. Russell and Cochran (66) investigated the adsorption of n-butane on different types of alumina and concluded that the correct cross-sectional area for the molecule is 39 sq. A. Livingston (64) has reviewed the literature on the adsorption of n-butane by inorganic materials and has stated that, if the nitrogen area is taken as a standard, 44.6 sq. A. is the "best area value" for the butane molecule. The present work indicates in a similar way that for cellulosic materials, 32.1 sq. A. is somewhat low for the molecular area of n-butane.

The Fu-Bartell area determined from the adsorption of n-butane on sprucewood is considerably lower than that determined by the other methods. It is also lower than the Fu-Bartell area computed from the nitrogen adsorption data. This latter difference is probably due to some extent to a smaller apparent porosity of the sprucewood with respect to the larger butane molecules than is the case when the adsorbate was nitrogen. The fact that the Fu-Bartell method fails to give areas of the adsorbents which are comparable with those determined by the B.E.T. and Harkins-Jura methods is no reflection on the validity of the method. It should be recalled that the Fu-Bartell technique is based on the assumption that the

adsorbent is highly porous. The results obtained in the present work demonstrate only that the method could not be successfully used to measure the area of essentially nonporous materials.

Thermodynamic Functions for the Adsorption of Nitrogen and n-Butane

Decrease in Free Surface Energy

Calculations were made of the decrease in free surface energy $-\Delta F$ for the adsorption of n-butane at 0°C. and nitrogen at -195.7°C. on the sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose. Equation (31) was employed and the indicated integration was carried out graphically. Harkins and Jura (67) have stated that there is only one procedure which makes it possible to obtain the correct value for this integral. This is to determine experimental points down to a relative pressure of approximately 0.001 to permit an accurate extrapolation to zero pressure. These necessary low-pressure data are given in Table J in the Appendix and are plotted in Figure 12. These isotherms in combination with those plotted in Figures 3 to 5 were used to evaluate the decrease in free surface energy. The specific surface area of each adsorbent which is necessary to determine the change in free surface energy was calculated with the B.E.T. equation from nitrogen adsorption data assuming a molecular area of 16.2 sq. A. Values of the decrease in free surface energy at various relative pressures for both nitrogen and n-butane are given in Table K in the Appendix and are plotted in Figures 13 to 15.

The shape of the free energy curves for nitrogen adsorption on all three materials is very similar. This is also true for n-butane. Values of the change in free surface energy at three arbitrarily selected relative pressures are given in

Table VIII.

TABLE VIII

DECREASE IN FREE SURFACE ENERGY

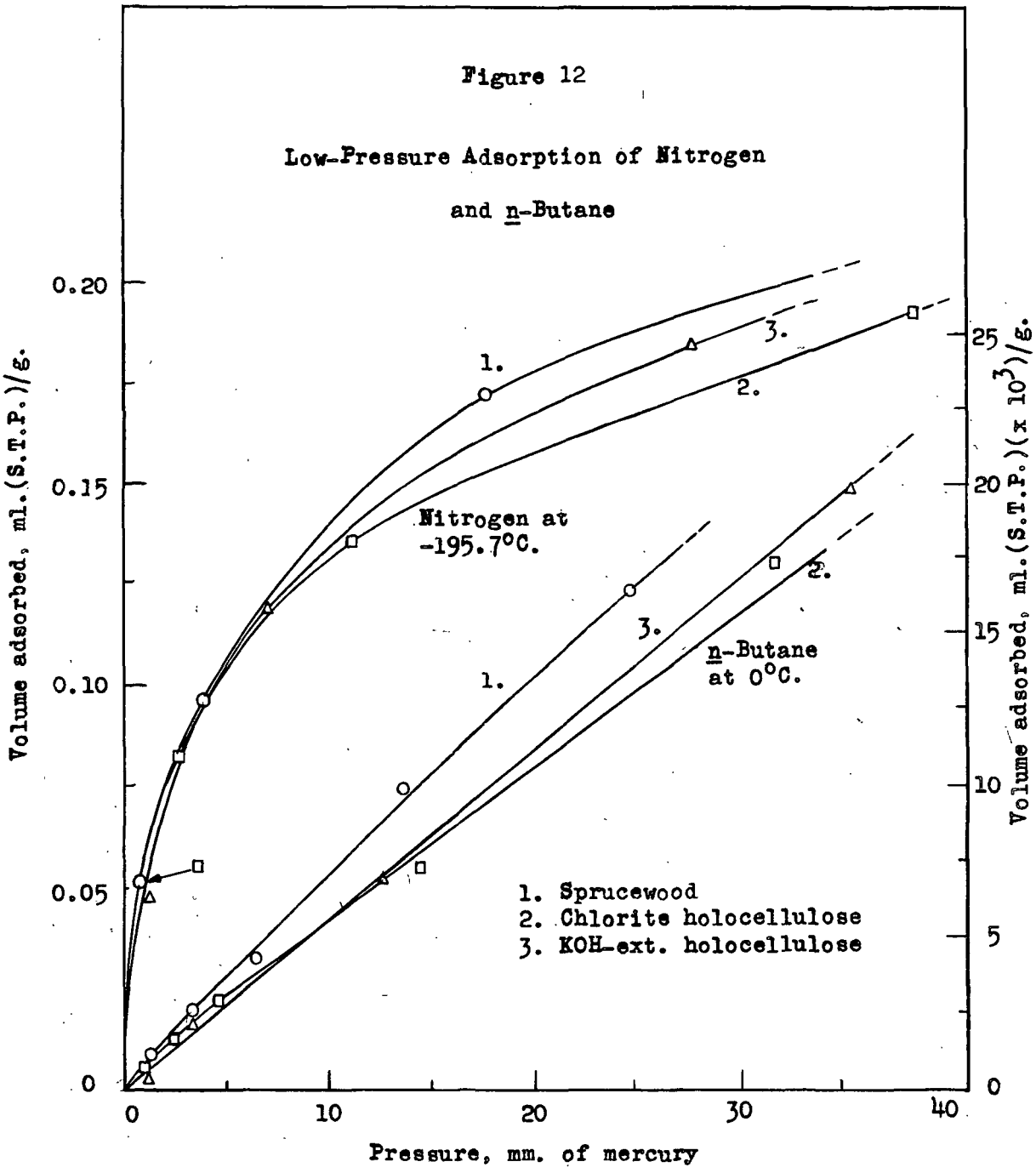
	$-\Delta F$, ergs per sq. cm.		
p / p_o	0.20	0.50	0.80
Nitrogen			
Sprucewood	22.0	30.8	37.0
Chlorite holocellulose	22.1	30.8	37.0
KOH-ext. holocellulose	22.4	30.8	36.9
n-Butane			
Sprucewood	8.2	17.4	25.9
Chlorite holocellulose	7.4	16.0	23.9
KOH-ext. holocellulose	7.5	16.5	25.2

For nitrogen, it is apparent that the decrease in free surface energy was almost exactly the same on the three adsorbents. The similar decrease for the adsorption of n-butane was also much the same for all three materials although somewhat less uniformity may be noted than in the case of nitrogen adsorption. In general, the adsorbed gas film was not appreciably influenced by changes in the chemical composition of the adsorbents and with either nitrogen or n-butane nothing more than physical adsorption was indicated.

Harkins and Jura (67) investigated the decrease in free surface energy for the adsorption of nitrogen and n-butane on a number of polar solids. In their work, the values at $p / p_o = 1.0$ always fell between 30 to 45 ergs per sq. cm. for n-butane at 0°C. and between 35 to 56 ergs per sq. cm. for nitrogen at -195.8°C. The respective values obtained by extrapolation of the curves in Figures 13 to 15

Figure 12

Low-Pressure Adsorption of Nitrogen and n-Butane



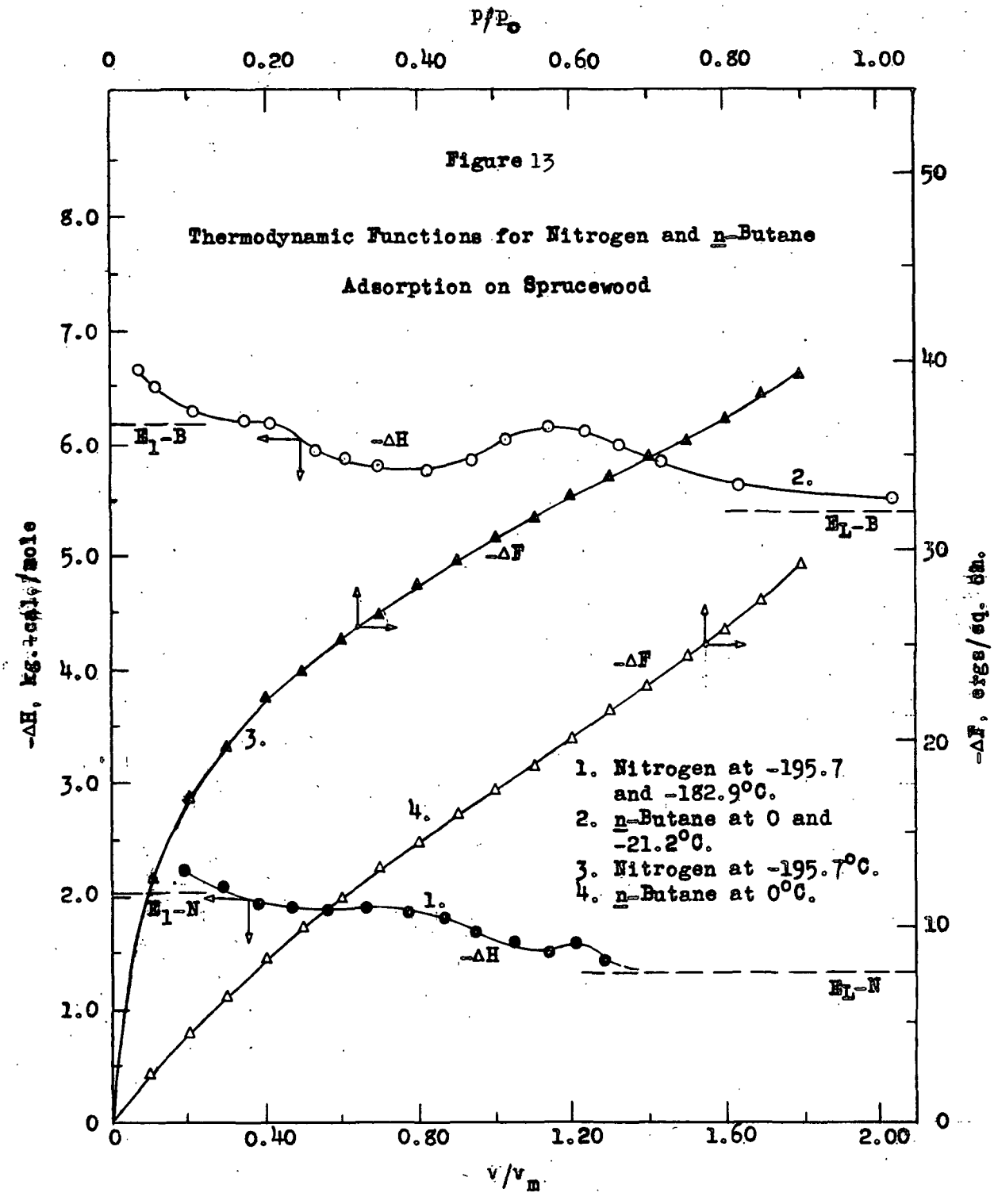


Figure 13

Thermodynamic Functions for Nitrogen and n-Butane Adsorption on Sprucewood

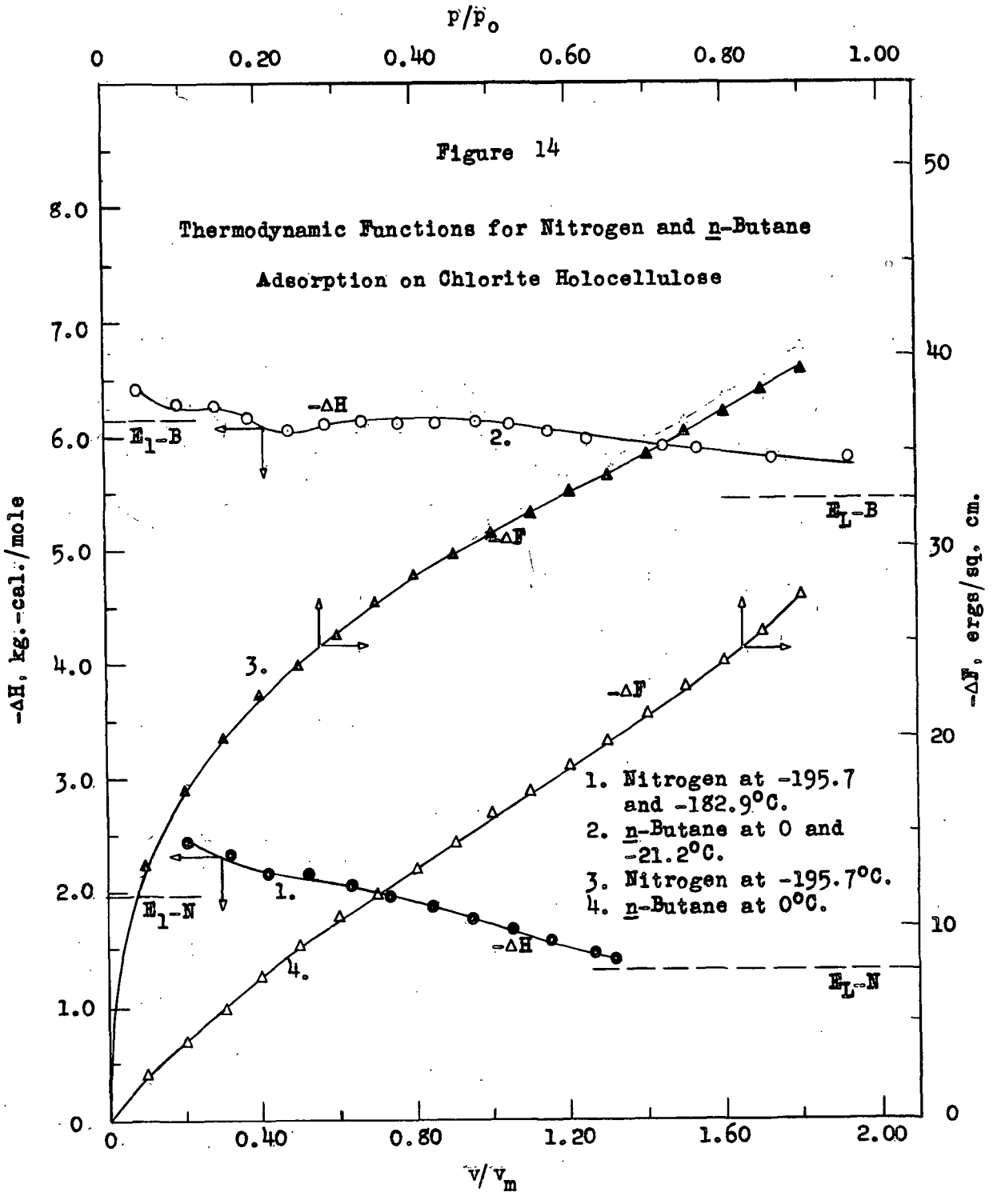


Figure 14

Thermodynamic Functions for Nitrogen and n-Butane Adsorption on Chlorite Holocellulose

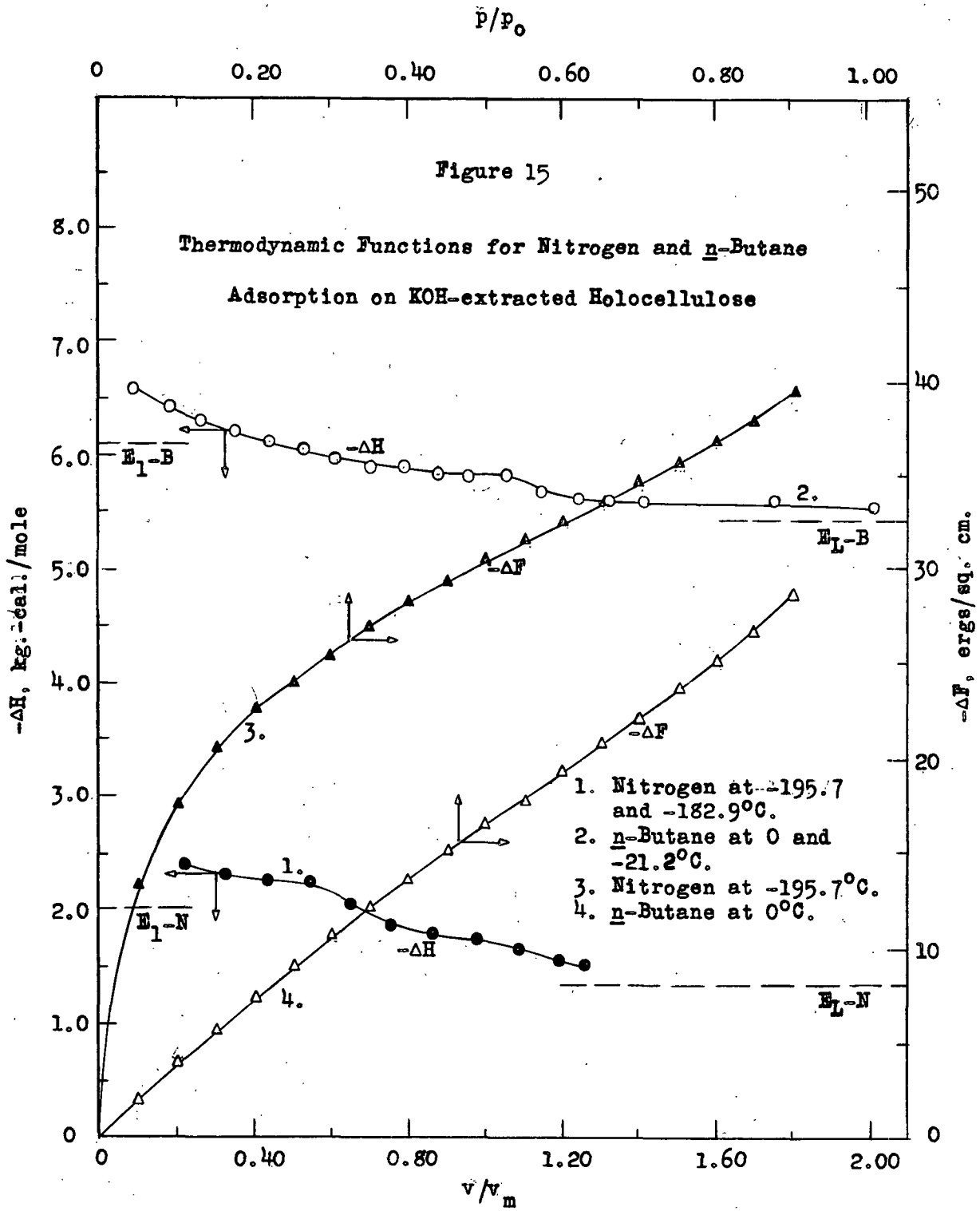


Figure 15

Thermodynamic Functions for Nitrogen and n-Butane Adsorption on KOH-extracted Holocellulose

also fall within these limits. The free energy changes for nitrogen determined in the present work are considerably different from those reported by Rowen and Blaine (32). These workers found a decrease in free surface energy at a relative pressure of 0.40 for the adsorption of nitrogen on cotton of 20 in comparison to approximately 28 ergs per sq. cm. for nitrogen on all the present adsorbents at this relative pressure. This difference does not appear to be due to a difference in the nature of the adsorption but rather to the fact that Rowen and Blaine neglected to take the necessary adsorption measurements at very low pressures.

Change in Differential Heat of Adsorption

Since adsorption is always an exothermic process, heat is liberated when a gas is adsorbed by a solid. If, for example, a thoroughly evacuated adsorbent weighing 1 gram is exposed to a gas, n moles of gas will be adsorbed and a certain amount of heat will be given off in the process. This quantity of heat is called the integral heat of adsorption. If the amount of adsorbed gas is then increased by dn, an additional amount of heat dq will be liberated. The differential coefficient $(\partial q / \partial n)_T$ is called the differential heat of adsorption ΔH.

Differential heats of adsorption on the sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose were calculated by the Clausius-Clapeyron equation from nitrogen adsorption determined at -195.7 and -182.9°C. and from n-butane adsorption at 0 and -21.2°C. These values, listed in Table L in the Appendix, are plotted against v / v_m, the relative portion of the adsorbent surface occupied by adsorbed molecules in Figures 13 to 15. (The v_m for each gas on each adsorbent was computed with the B.E.T. equation.)

In all cases the differential heat of adsorption approaches E_L, (E_L - B for n-butane and E_L - N for nitrogen) which here represents the average heat of liquefaction of the particular adsorbate at the two temperatures at which the isotherms were measured. Although apparently not the case for n-butane, the nitrogen heat curves would probably exhibit a sharp decrease from somewhat higher values for the first small amount of adsorption. This cannot be determined with certainty because it was not possible to calculate accurate heat values for nitrogen below $v / v_m = 0.20$ since the pressures of less than 0.8 mm. involved could only be measured to $\pm$ 0.1 mm. with the cathetometer.

In no instance do the curves for $-\Delta H$ decrease smoothly as adsorption proceeds. This is especially true for the heat calculated for the adsorption of n-butane on sprucewood. Here an increase in $-\Delta H$ to give a peak at approximately $v / v_m = 1.2$ occurs. Although a very broad rise occurs in the curve for n-butane adsorption on chlorite holocellulose, generally for this material and for the alkali-extracted chlorite holocellulose, the curves for $-\Delta H$ decrease somewhat more smoothly than for sprucewood.

Humps in differential heat of adsorption curves are not common but have been previously reported by other workers. Zettlemoyer, Chand, and Gamble (68), when investigating the adsorption of nitrogen on polyethylene, found such a hump at a v / v_m value of 1.5. No attempt was made to explain this phenomenon. Joyner and Emmett (21) using isotherm data, and Beebe, Biscoe, Smith, and Wendell (69) using calorimetric means, have investigated the differential heat of adsorption of nitrogen on identical samples of carbon black. A hump was noted, in both cases, in the neighborhood of $v / v_m = 0.70$. It was the opinion of these workers that dispersion forces due to the lateral interaction of the adsorbed molecules were responsible for the

observed increase in the heat of adsorption where the hump occurred.

If dispersion forces of this type are the cause of the humps noted in the sprucewood curve, it is rather difficult to explain why humps do not occur in all the heat curves. This is especially true since the decrease in free surface energy which is related to the compressibility and the interaction of the molecules in the adsorbed film has already been shown to be similar for all three adsorbents. Rather, the fact that marked humps are noted for both n-butane and nitrogen only on the slightly porous sprucewood at essentially the same fractional coverage would seem to indicate that it is differences in submicroscopic structure that are responsible for the irregularities in the change of the differential heat of adsorption.

It will be recalled that Equations (19) and (21) permit calculation of $\underline{E}_1 - \underline{E}_L$, the difference between the heat of liquefaction and the average heat of adsorption in the first layer. This value has been computed for several of the nitrogen and n-butane isotherms. For nitrogen, it is essentially the same for all adsorbents and equal to approximately 665 cal. per mole. For n-butane, the difference is 835 for the sprucewood, 783 for the chlorite holocellulose, and 721 cal. per mole for the alkali-extracted chlorite holocellulose. Thus a small but definite decrease is noted as noncellulosic components are removed from the original wood. If $\underline{E}_L$ is taken as the average heat previously discussed, $\underline{E}_1$ has values as given in Figures 13 to 15. For n-butane, $\underline{E}_1$ appears to be a rather good estimate of the average heat of adsorption in the first layer as computed by the Clausius-Clapeyron equation. For nitrogen, $\underline{E}_1$ also checks quite well for the average of the heat curve for $\underline{v} / \underline{v}_m$ = 0.20 to 1.00. It would probably prove to give a somewhat low estimate, however, if the nitrogen heat information were available below $\underline{v} / \underline{v}_m$ = 0.20.

In general, the values found for the differential heats of adsorption were similar in magnitude to those commonly associated with van der Waals' adsorption. This study of the heats of adsorption served to confirm what was also indicated by the investigation of the change in free energy, namely, that the nitrogen and n-butane show no tendency to be more than physically adsorbed on wood and its components.

EQUILIBRIUM STUDIES WITH CARBON DIOXIDE

Early in the initial attempt to determine the adsorption isotherm of carbon dioxide on sprucewood at -78.6°C., it was noted that equilibrium was not quickly reached as had been the experience with nitrogen and n-butane. Therefore, a series of equilibrium studies were undertaken of the adsorption of carbon dioxide on samples of sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose.

These studies were carried out by first evacuating the specimen bulb in the normal fashion and immersing it in a Dry Ice-ether bath. A quantity of carbon dioxide was admitted to the evacuated buret system, and the pressure was measured. Expansion of the gas into the adsorption bulb was permitted; the time was noted; and manometer, buret temperature, and time readings were taken simultaneously at various times for a period of several days. All pressure readings were corrected to 25°C. and were plotted against time in minutes (log scale) in Figure 16. It should be noted that it is only the change in pressure with time that is important since no attempt was made to have the pressure the same at the beginning of each run. Following thorough evacuation, second equilibrium determinations were made for the adsorption of carbon dioxide on the sprucewood and the chlorite holocellulose. Numerical values for all curves are given in Table M in the Appendix.

It is apparent from Figure 16 that after approximately three-days exposure of the sprucewood and the chlorite holocellulose to carbon dioxide, the takeup was not at equilibrium nor is there any suggestion of a leveling out of the curves. In marked contrast to this, when the adsorbent was KOH-extracted chlorite holocellulose, equilibrium was reached in less than fifteen minutes.

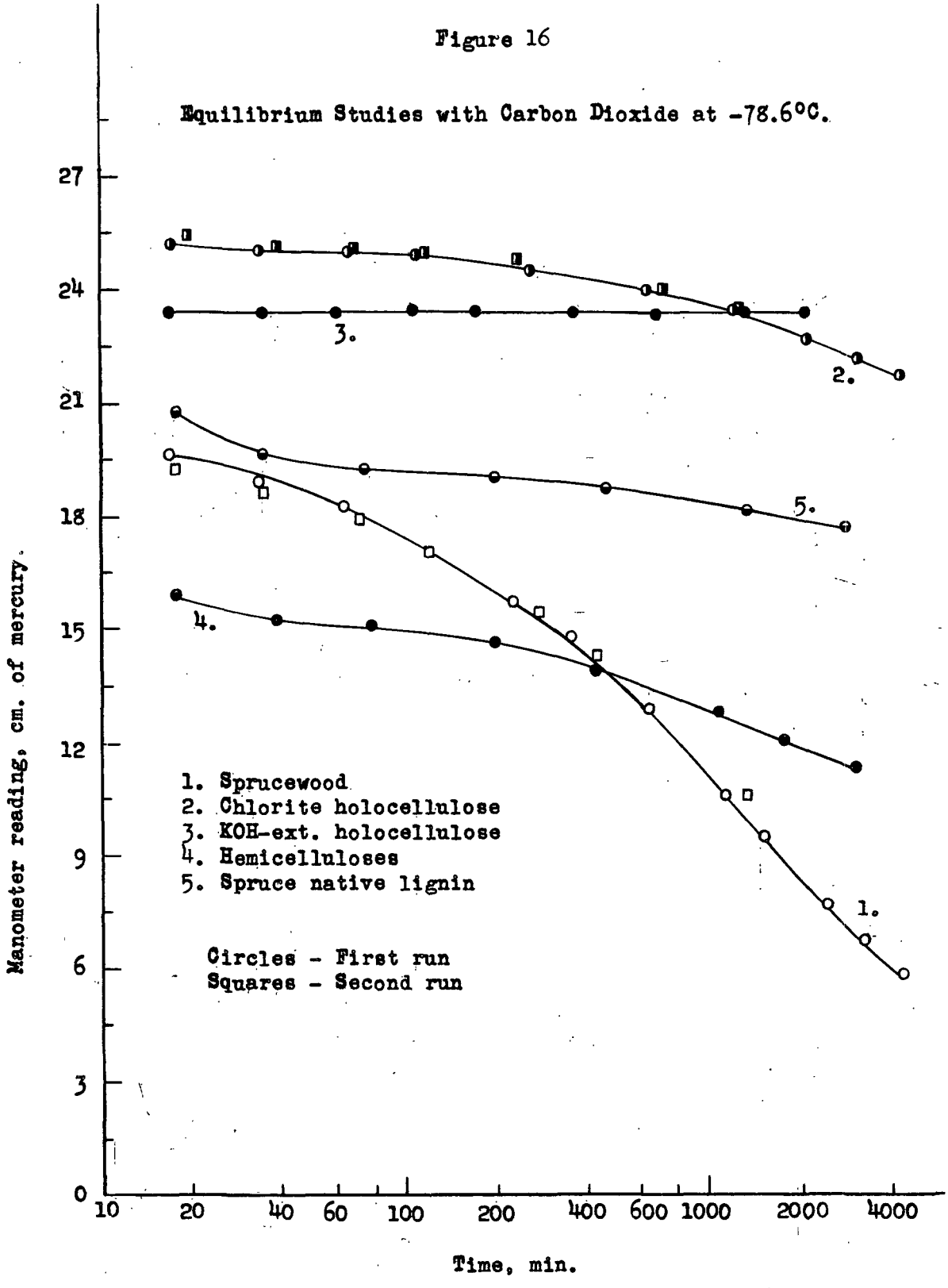
These results strongly indicated that the lignin or the hemicelluloses or possibly both materials which were to a large extent removed from the sprucewood during the chloriting and alkali-extraction operation may be responsible for the observed failure of the carbon dioxide to come to equilibrium. In order to investigate this possibility further, the caustic extract of the chlorite holocellulose was acidified and the hemicelluloses precipitated with ethanol in the manner described by Wise, Murphy, and D'Addieco (58). Following drying, the hemicelluloses were sealed in an adsorption bulb and a carbon dioxide equilibrium curve determined. A similar investigation was also made of the takeup of carbon dioxide at -78.6°C. on spruce native lignin.[1] The resulting curves are plotted in Figure 16 and it is observed that for the hemicelluloses and native lignin as for the sprucewood and chlorite holocellulose, the adsorption of carbon dioxide does not quickly attain equilibrium.

Salley (29) studied the adsorption of carbon dioxide by beaten bleached sulfite pulp and found that at 80°C. two days were required to reach equilibrium, at 56°C. eight days were necessary, whereas at 0°C. equilibrium still had not been reached after three weeks. Equilibrium was obtained at 0°C., however, when the adsorbent was cotton although the time required was not given. It is indicated both from

1 Acknowledgement is made to Dr. Brauns for the loan of a sample of black spruce native lignin.

Figure 16

Equilibrium Studies with Carbon Dioxide at -78.6°C.



this work and from the present study that, for carbon dioxide adsorption on cellulosic materials at lower temperatures, equilibrium was reached rapidly only when the adsorbent contained a high proportion of cellulose i.e., cotton or KOH-extracted chlorite holocellulose. For pulp, wood, and chlorite holocellulose and also for precipitated hemicelluloses and native lignin, equilibrium was not obtained after 2 to 3 days. It would appear fairly certain then that it is the noncellulosic constituents of the wood that are responsible for the observed prolonged takeup of carbon dioxide at low temperatures.

It is generally considered that in physical adsorption, the gas molecules are adsorbed as rapidly as they can reach the surface. Therefore, for nonporous solids, adsorption equilibrium is usually reached in a matter of minutes or at the most a few hours. It is apparent then that, when the adsorbate is carbon dioxide at $-78.6^{\circ}C.$, something in addition to physical adsorption on the external surface of the sprucewood and chlorite holocellulose is taking place for, equilibrium was not reached after three days. In addition, it was noted that considerably more carbon dioxide is taken up than the external area of these materials would warrant.

The phenomena other than physical adsorption which could be responsible for the prolonged uptake of carbon dioxide include chemisorption, solution, or alteration of the area of the adsorbent by the gas. Since the powdered hemicelluloses and native lignin behave much the same as the sprucewood and the chlorite holocellulose toward carbon dioxide, indications are that an alteration of area is not wholly responsible. It was considered, however, as a possible contributing factor. That is, it was thought that the adsorbed carbon dioxide might slowly act on the sprucewood (or chlorite holocellulose) in such a way as to open up and make available for further adsorption a portion of the large internal area closed off when the material

was dried from water. To test this idea, sprucewood which had been exposed to carbon dioxide for several days was evacuated first at -78.6°C. and then at room temperature. The area of the sprucewood treated in this manner was determined using nitrogen adsorption data and was found to be exactly the same as for a sprucewood sample unexposed to carbon dioxide. Since it does not seem likely that the evacuation of the adsorbed carbon dioxide would completely reverse any area change, it is more probable that the area was never altered.

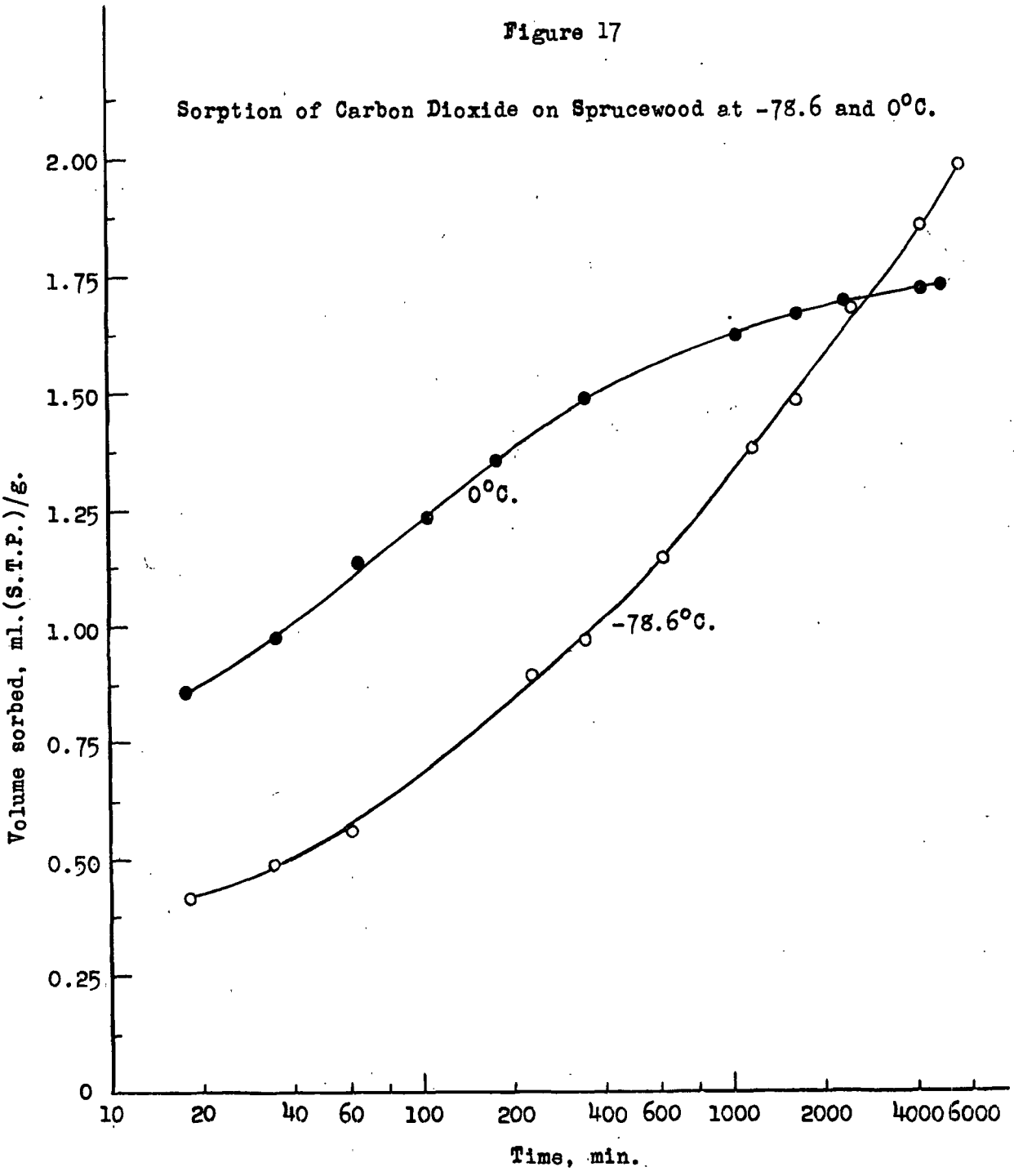
To provide further information on the carbon dioxide-sprucewood system, the rate of uptake of gas at 0°C. was determined. The volume of carbon dioxide sorbed at both 0 and -78.6°C. is plotted against time in minutes (log scale) in Figure 17 (Table N - Appendix). Although the initial rate of gas uptake is more at 0°C. than at -78.6°C., the volume sorbed is greater for the lower temperature at the longer times of exposure. In addition, although equilibrium was not reached at 0°C. after four days, it was being approached, and the sorption rate had decreased to a much smaller value than after the same time at -78.6°C. Use was made of these rate data to calculate $\underline{E}$, the activation energy employing an integrated modified Arrhenius equation suggested by Taylor and Williamson (70). This equation is

$$\log \underline{v}_2 - \log \underline{v}_1 = \frac{\underline{E}}{4.58} \left(\frac{1}{\underline{T}_1} - \frac{1}{\underline{T}_2}\right) \qquad (44)$$

where $\underline{v}_2$ and $\underline{v}_1$ are the sorption velocities corresponding to the respective temperatures $\underline{T}_2$ and $\underline{T}_1$. The value of $\underline{E}$ calculated from Equation (44) for the initial sorption of carbon dioxide on sprucewood is of the order of 2 kg. cal. per mole. This is considerably lower than the values generally associated with a chemical reaction. Also, the fact that $\underline{E}$ becomes negative at longer times demonstrates the fallaciousness of even applying such an equation in the present case. For

Figure 17

Sorption of Carbon Dioxide on Sprucewood at -78.6 and 0°C.



these reasons, it does not appear that chemical reaction was occurring.

Brunauer (1) has suggested that a long continued uptake of gas is due usually to solution in the solid rather than to adsorption alone. Such a solution of gas has been proposed by Bangham and Sever (71) in explanation of a prolonged uptake of carbon dioxide by glass noted by Bangham and Burt (72). It may very well be that a similar solution of carbon dioxide is taking place in the hemicelluloses and the lignin present in the sprucewood and the chlorite holocellulose. The finding that following evacuation the second takeup of gas by the sprucewood and chlorite holocellulose samples was similar to the initial sorption would be compatible with the occurrence of such solution. Although it is not impossible that an alteration of area is occurring, it seems more likely that a combination of rapid physical adsorption followed by a very slow solution of the carbon dioxide by the noncellulosic constituents of the sprucewood accounts for the observed prolonged sorption of the gas.

ADSORPTION OF CARBON DIOXIDE ON KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Since the adsorption of carbon dioxide on the sprucewood and chlorite holocellulose samples does not reach equilibrium in a reasonable time at -78.6°C., adsorption studies with this gas could be made only on the KOH-extracted holocellulose.

Adsorption-Desorption Isotherms

Isotherm data for the adsorption and desorption of carbon dioxide on KOH-extracted holocellulose at -78.6°C. are given in Table O in the Appendix. These isotherms are also plotted in Figure 18. In addition to the data for the initial exposure of the material to carbon dioxide, points are also included for a second

run made on the same sample following thorough evacuation at room temperature. The isotherms are essentially the same for the first and second runs. In contrast to isotherms obtained when n-butane or nitrogen was the adsorbate, the desorption isotherm for carbon dioxide at no point became identical with the adsorption loop. Indications are, however, from the low-pressure points on the desorption curve, that as the pressure is decreased more and more the quantity of adsorbed carbon dioxide will approach zero. This is also indirectly indicated by the duplication of the first and second adsorption curves since if the initially adsorbed gas was not wholly removed on evacuation, the second adsorption could be expected to be somewhat less than the first. Therefore, although not strictly reversible by small changes in pressure, the adsorbed carbon dioxide is apparently wholly removed by evacuation. This is in agreement with the observation of Grace and Maass (28) that carbon dioxide adsorbed by sprucewood could be readily desorbed on evacuation.

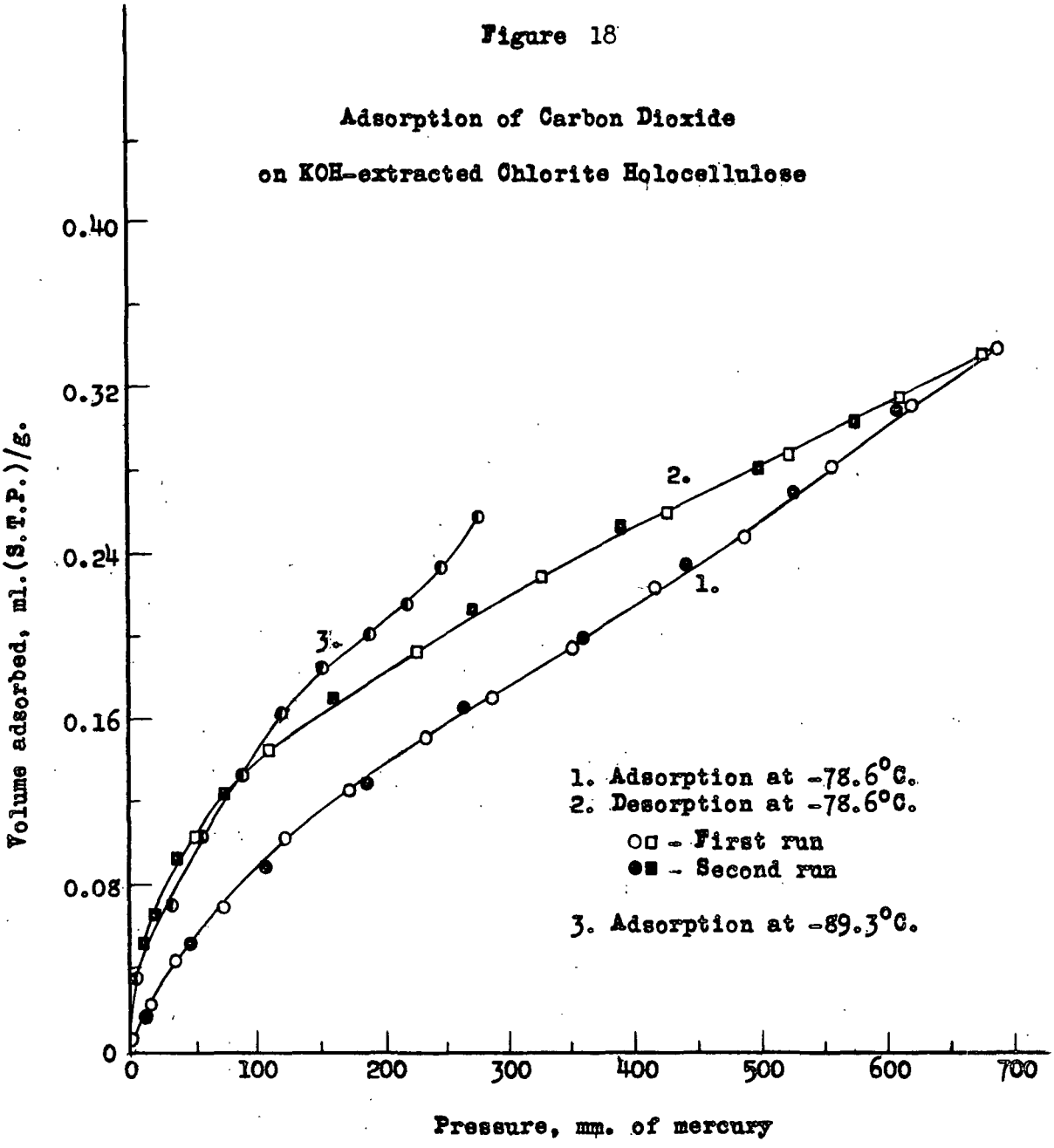
The large hysteresis loop which was obtained may be due to a somewhat stronger attraction occurring between the adsorbed carbon dioxide and the adsorbent than existed when nitrogen or n-butane was the adsorbate. Such an increased attraction could result from hydrogen bonding occurring between the oxygens of the carbon dioxide molecules and the uncombined cellulosic hydroxyl groups. If such is the situation, it might very logically be expected to result in a high initial differential heat of adsorption. That such is the case will be subsequently shown.

Computation of the monolayer volume by the B.E.T. method for the adsorption of carbon dioxide on the KOH-extracted holocellulose reveals that the area occupied by a single adsorbed carbon dioxide molecule was 28.3 or 27.5 sq. A. depending on whether an area of 16.2 or 15.7 sq. A. was assigned as the area of a nitrogen molecule. These values are somewhat higher than the 19 to 20 sq. A. reported by

Figure 18

Adsorption of Carbon Dioxide

on KOH-extracted Chlorite Holocellulose



Livingston (64) to be the molecular area for carbon dioxide adsorbed on porous glass and silica gel. It should be recognized, however, that these siliceous materials are markedly different from the organic, nonporous (when dried from water), KOH-extracted chlorite holocellulose which is the adsorbent being studied in the present work. If, as has been postulated, the carbon dioxide molecules are particularly attracted to the surface hydroxyl groups of the cellulose, it is very probable that the movement of the adsorbed molecules on the surface of the adsorbent is restricted. If such is the case, the adsorbed gas molecules are not free to move in a manner which is necessary if they are to fit together to form a continuous monomolecular film. Rather, spaces or gaps may exist between the firmly held carbon dioxide molecules which are too small to be filled by a molecule adsorbed directly from the gas phase and hence remain unoccupied. In this way, the effective area of a carbon dioxide molecule adsorbed on cellulose would be somewhat greater than that observed for inorganic materials.

Thermodynamic Functions

The decrease in the free surface energy occurring on the adsorption of carbon dioxide by the KOH-extracted chlorite holocellulose at -78.6°C. is given in Table P in the Appendix and in Figure 19 is plotted against the relative pressure. This function was calculated from the adsorption data in the manner previously described. The curve for decrease in free surface energy is similar in shape and magnitude to corresponding curves obtained when the adsorbate was nitrogen or n-butane.

Values (see Table P in Appendix) for the differential heat of adsorption of carbon dioxide on KOH-extracted chlorite holocellulose computed from isotherms measured at -78.6 and -89.3°C. are plotted in Figure 19 against v / v_m, the relative

portion of the surface occupied by adsorbed gas. It is apparent that relatively high heats are involved for the initial quantities of gas adsorbed. The values (7 to 10 kg. -cal. per mole) calculated for $\underline{v} / \underline{v}_m = 0.20$ or less, are considerably higher than the corresponding differential heats computed for the adsorption of nitrogen or n-butane on the same adsorbent. Since the energy value generally associated with hydrogen bonds is 5 to 10 kg. -cal. per mole (73), it is not unreasonable to believe that these high initial heats may be due to this cause. Most certainly, the values obtained for the heat of adsorption would tend to support rather than disprove the contention discussed earlier that the hysteresis noted during desorption may be due to the occurrence of hydrogen bonding.

The differential heat of adsorption first decreased quite rapidly and then more slowly with increased adsorption approaching 4.1 kg. -cal. per mole at the highest adsorbed volumes. This final heat value is considerably different from 6.1 kg. -cal. per mole, which is the heat of sublimation of solid carbon dioxide at -84°C., the average of the two temperatures at which isotherms were measured (74). Interestingly enough, if the liquid carbon dioxide line on a chart of the properties of carbon dioxide prepared by Refrigeration Engineering (74) is extrapolated to the saturation pressure at -84°C., a value of approximately 4.1 kg. -cal. per mole is obtained. This similarity between the final calculated differential heat of adsorption and an extrapolated "heat of liquefaction" of carbon dioxide may be only coincidence but also it may indicate that at the low temperatures employed the second and higher adsorbed layers of carbon dioxide exist in a state corresponding more closely to a liquid than a solid.

Calculation of $\underline{E}_1 - \underline{E}_L$ using the B.E.T. theory for the adsorption of carbon dioxide on the KOH-extracted chlorite holocellulose gives a value of 845 cal. per

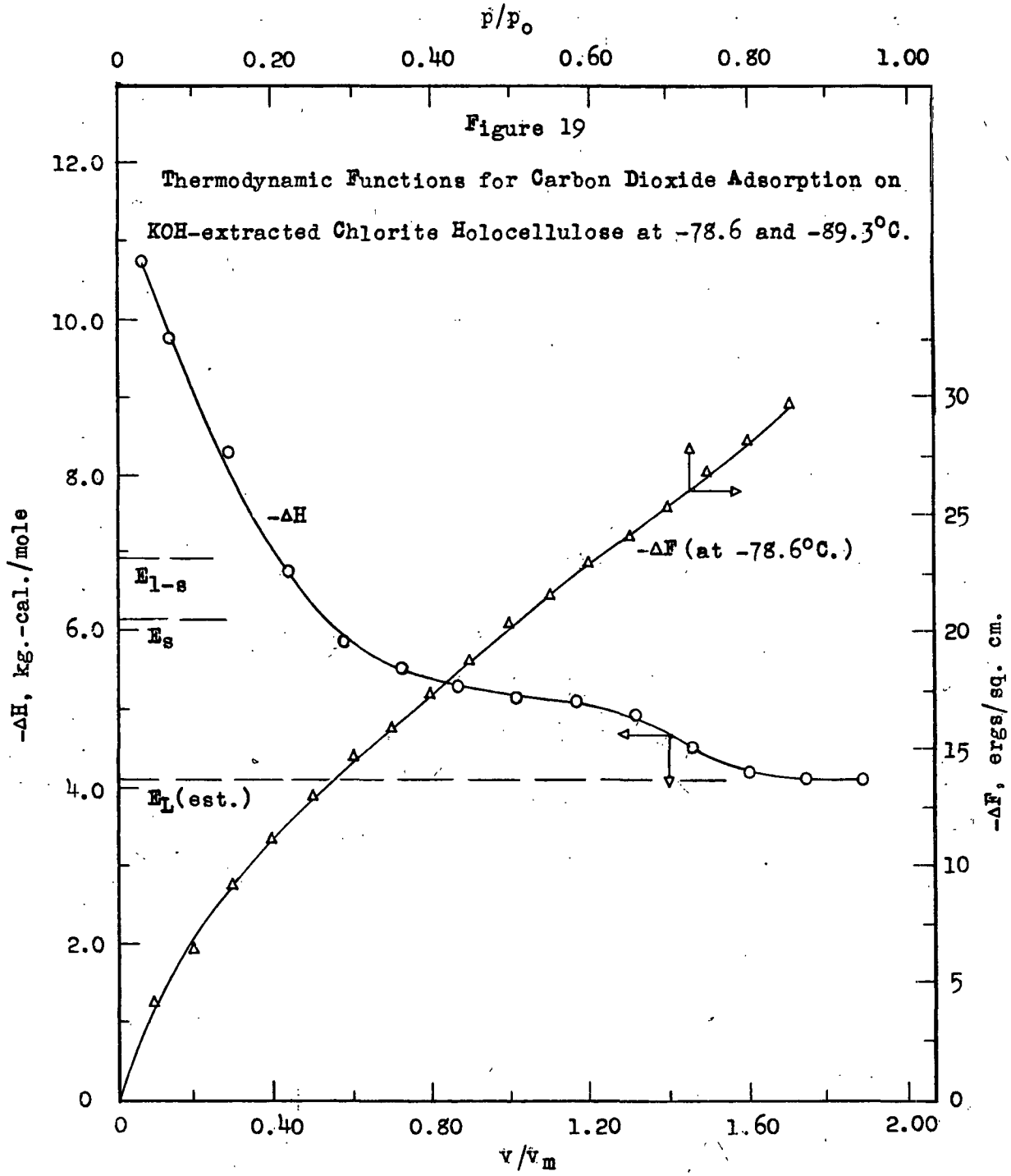


Figure 19

Thermodynamic Functions for Carbon Dioxide Adsorption on KOH-extracted Chlorite Holocellulose at -78.6 and -89.3°C.

mole. $\underline{E}_1$ has been plotted in Figure 19 assuming $\underline{E}_L$ to be the heat of sublimation of solid carbon dioxide $\underline{E}_s$ at -84°C. When this is done, it appears that $\underline{E}_{1-s}$ provides a good estimate of the average heat of adsorption of the first layer. Heat considerations indicate, therefore, that the carbon dioxide molecules in the first layer act as if their condition was that of a "solid" state whereas for the second and higher layers of adsorbed gas, a "liquid" condition is suggested.

When the adsorption studies which have been made on sprucewood and its components are reviewed, it is seen that the nature of the adsorption of both n-butane and nitrogen is such that either gas can be used for area measurements on cellulosic materials. Carbon dioxide, however, appears to be soluble in the noncellulosic constituents of wood and for this reason not suitable for area studies when these materials are present. Even when the adsorbent contains a high percentage of cellulose and equilibrium adsorption is quickly reached, carbon dioxide is not to be recommended for area measurements since isotherm and differential heat considerations indicated that hydrogen bonding of the adsorbed gas molecules may be occurring. Of the two gases, nitrogen has several advantages over n-butane. The smaller, more-spherical molecules of nitrogen have an area which is more definitely known. Nitrogen does not require correction for deviation from the perfect gas laws at room temperature, and also it generally gives adsorption measurements and area plots having slightly better precision.

Both the B.E.T. and the Harkins-Jura methods of computing surface area have been shown to give satisfactory results when applied to adsorption data measured on cellulosic materials. In actual practice, however, the B.E.T. method seems more desirable to use since it gives better straight line plots and requires the measurement of fewer points on the adsorption isotherm than does the Harkins-Jura method.

It appears that nitrogen adsorption measurements and the B.E.T. method of computing area constitute the best combination for area studies of pulp and paper using gas adsorption techniques.

INVESTIGATION OF THE INTERNAL AREA AND STRUCTURE OF BENZENE-DRIED SPRUCEWOOD, CHLORITE HOLOCELLULOSE, AND KOH-EXTRACTED CHLORITE HOLOCELLULOSE

The work of Hunt, Blaine, and Rowen (34) has convincingly demonstrated that many of the minute pores and longitudinal submicroscopic channels exposed in wet cotton can be preserved in the dry material by displacement of the water and drying from a nonpolar organic solvent such as benzene. Samples of the sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose were subjected to this treatment and the nature of the nitrogen adsorption and desorption isotherms at -195.7°C. on each material was determined. From these data, the area of each sample was computed by the B.E.T. method, and pore volume distribution curves were determined for the chlorite holocellulose and the KOH-extracted chlorite holocellulose by the method of Wheeler and Shull (37). Samples of benzene-dried, alkali-extracted chlorite holocellulose were then allowed to absorb various amounts of moisture by exposure to different relative humidities and the effect of this moisture takeup on the accessible internal area was studied.

EXPERIMENTAL PROCEDURES

PREPARATION OF SAMPLES

The procedure described by Assaf, Haas, and Purves (31) was employed for the preparation of the porous samples for adsorption, area, and pore volume distribution studies. Approximately 10 g. each of 40- to 60-mesh sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose were soaked in distilled water for 12 hours. Each sample was drained on a coarse fritted-glass funnel just until there was no free liquid standing above the material. (In no case while draining or handling was a portion of the sample allowed to dry out even superficially until

after the final treatment with benzene.) The drained water-wet material was stirred in 2/3 liter of 99 + methanol and was allowed to stand for 20 minutes with occasional stirring. The sample was filtered and the operation was repeated with fresh 99 + methanol and then with methanol which had been dried by distillation over magnesium. The displacement of the methanol was next accomplished by stirring the sample in 2/3 liter of thiophene-free benzene which had been dried by distillation and storage over metallic sodium. After a period of 40 minutes, the sample was redispersed in a fresh charge of benzene. Following this final treatment, the benzene was thoroughly drained from the material which was placed in a vacuum desiccator over calcium chloride and paraffin wax. The desiccator was evacuated periodically to not lower than 3 mm. of mercury. (Lower pressures were avoided to minimize the chance of collapsing the internal fiber structure due to over-rapid or irregular evaporation of the benzene.) Approximately one week was required to remove the benzene in this manner. After storing all samples over phosphoric anhydride for several days, approximately 1.5 g. of each material were sealed, as quickly as possible, into standard adsorption bulbs.

In preparing the benzene-dried, KOH-extracted chlorite holocellulose for moisture absorption-accessible area studies, the original water-dried, 40- to 60-mesh material was initially passed through an Abbé defibrator. The product was screened through a 40-mesh sieve with that portion which would pass a 100-mesh sieve being rejected. A part of this material was set aside and the remainder (approximately 50 g.) was treated with methanol and benzene in the manner previously described with appropriate increases in the quantities of the solvents.

EXPOSURE OF BENZENE-DRIED, KOH-EXTRACTED CHLORITE HOLOCELLULOSE TO VARIOUS RELATIVE HUMIDITIES

Appropriately sized portions of the benzene-dried, KOH-extracted chlorite holocellulose were exposed to the various relative humidities listed in Table IX until equilibrium takeup of moisture was reached. Relative humidities up to 92.9% were maintained by means of several of the saturated salt solutions listed by Wink (75). To obtain a relative humidity of 96.7%, a saturated solution of sodium fluoride (76) was used, whereas for maintenance of 99.6% R.H., a 1.1% solution of sulfuric acid was employed (77).

TABLE IX

RELATIVE HUMIDITIES EMPLOYED IN AREA STUDIES ON BENZENE-DRIED, KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Relative Humidity at 73°F., %	Solution Employed
22.9	Potassium acetate saturated solution
58.5	Sodium bromide saturated solution
86.5	Potassium chromate saturated solution
92.9	Ammonium monophosphate saturated solution
96.7	Sodium fluoride saturated solution
99.6	1.1% sulfuric acid solution

Exposure of the benzene-dried samples to relative humidities of 86.5% and lower was carried out in glass dish units of the type described by Wink (75). These units were kept in a room maintained at 73°F. For exposure to 92.9% R.H. and above, a more specialized procedure was used to prevent condensation and to speed the attainment of equilibrium. Approximately 8 g. of sample were placed in each of three 22 mm. glass tubes. These were fitted at either end with stoppers and glass tubes and were placed in a large insulated box in a room kept at 73°F.

Also contained in the box were small suction flasks containing the proper solution to obtain the desired relative humidity. Each of the three flasks was connected by rubber tubing through a Sigmamotor tubing pump to one of the three tubes containing the benzene-dried samples. When the pump was in operation, a closed air system was continually circulated through the pump, constant humidity solution, sample, and back to the pump. The cabinet was equipped with a front glass window, two small openings on either side of the window which had been fitted with rubber gloves and polyethylene sleeves, and an analytical balance on top with a wire extending down into the box. The sample tubes were weighed periodically to determine when equilibrium was reached without removing them from the cabinet. This was done by reaching into the cabinet with the rubber gloves, disconnecting the rubber tubing, sealing the ends of the tube with medicine dropper bulbs and hanging the tube on the wire extension of the balance. Two to three weeks were required to reach equilibrium at the higher relative humidities.

Following exposure, the moisture regained by each sample was determined. After drying each material for five days in an evacuated desiccator over phosphoric anhydride, the samples were sealed in adsorption bulbs and their area was measured by nitrogen adsorption.

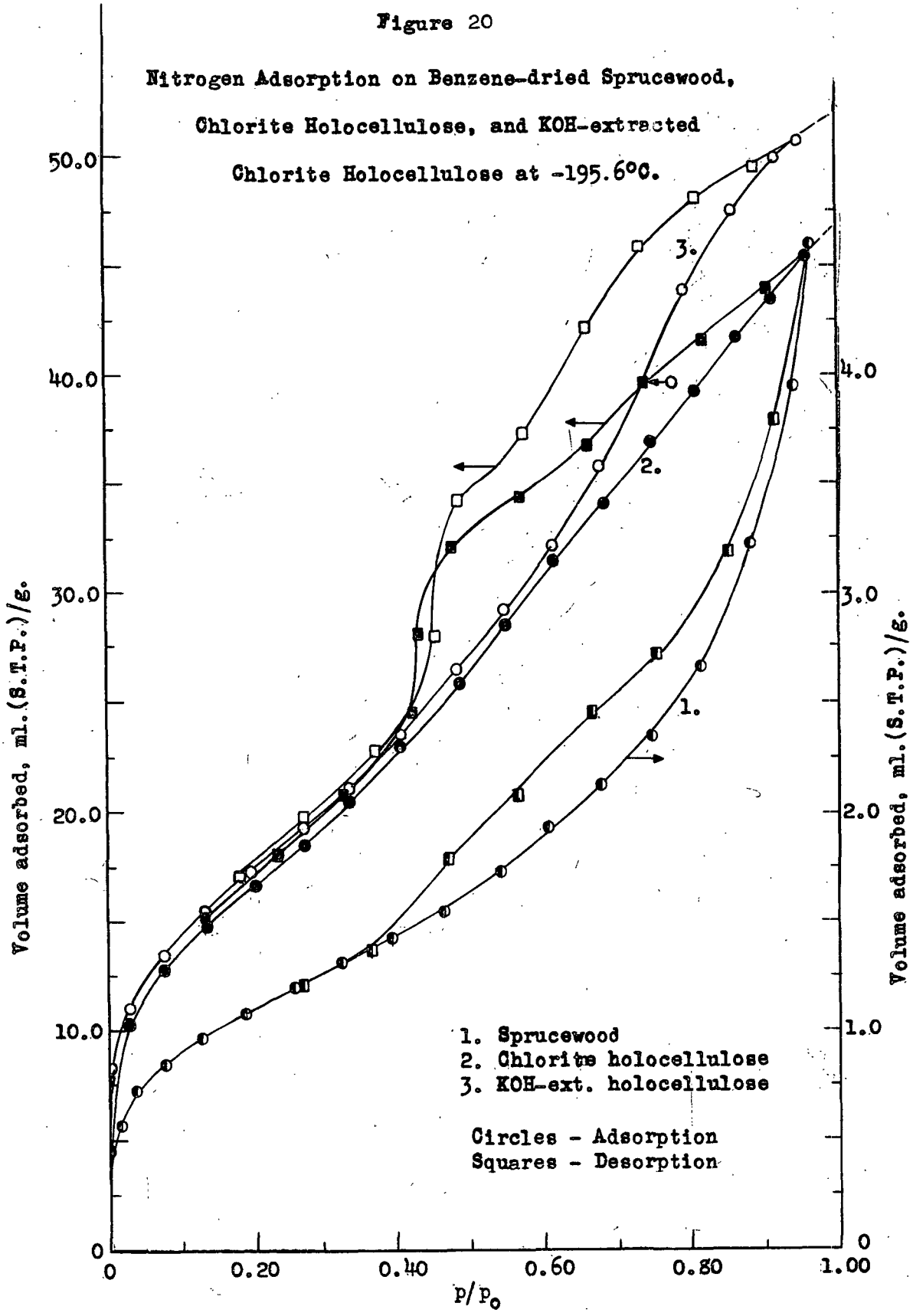
EXPERIMENTAL RESULTS AND DISCUSSION

NITROGEN ADSORPTION AND DESORPTION ISOTHERMS

Data for the adsorption of nitrogen at -195.6°C. on benzene-dried sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose are given in Table Q in the Appendix. These data are also plotted against relative pressure in Figure 20. It is noted that the volume of gas adsorbed is appreciably greater than for the same materials which have been dried from water. (The benzene-dried

Figure 20

Nitrogen Adsorption on Benzene-dried Sprucewood, Chlorite Holocellulose, and KOH-extracted Chlorite Holocellulose at -195.6°C.



samples are the same as those on which the original nitrogen adsorption work was done except for the state of subdivision and the manner of drying. These present samples were prepared from the 40- to 60-mesh products which were ground to pass a 120-mesh screen for the earlier work.)

The adsorption isotherm obtained when the adsorbent was sprucewood dried from benzene was S-shaped and similar to that found for the water-dried sprucewood. However, the hysteresis loop obtained in the present study was considerably larger. The area available for adsorption as measured by the B.E.T. method (nitrogen molecular area; 16.2 sq. A.) is 4.0 sq. m. per gram. Although the operation of soaking in water and drying from benzene after solvent displacement of the water rendered a portion of the internal area accessible to the gas, the effect was much less than for the chlorite and KOH-extracted holocellulose which had areas of 61.3 and 62.2 sq. m. per gram, respectively. It seems likely that the wood particles, stiffened as they are by the lignin present, were not swollen in water to the extent that the more purified materials were and, therefore, did not possess a very high accessible internal area when dried from benzene. There is also the strong possibility, as has been suggested by Frey-Wyssling (78), that a portion of the spaces between the microfibrils and the micelles in the wood are filled in or occluded by the lignin.

The adsorption-desorption curves for the benzene-dried samples of the chlorite holocellulose and KOH-extracted chlorite holocellulose are examples of isotherms which have been termed type IV by Brunauer, Deming, Deming, and Teller (16). The peculiar shape of the large hysteresis loops of such curves is indicative of a highly porous adsorbent. The isotherms obtained in the present work are quite similar to those found by Hunt, Blaine, and Rowen (34) for nitrogen adsorption on

benzene-dried cotton linters.

PORE VOLUME DISTRIBUTION OF THE BENZENE-DRIED CHLORITE AND KOH-EXTRACTED HOLOCELLULOSE

The pore volume distribution of the benzene-dried chlorite and KOH-extracted holocellulose was determined from the nitrogen adsorption data employing the method of Wheeler and Shull (37) already discussed in detail in the Historical Review. It was not possible to obtain a similar distribution for the sprucewood due to the uncertainty involved in extrapolating an S-shaped isotherm to saturation pressure. For these determinations, the adsorption curves were employed instead of those obtained on desorption as was done by Hunt, Blaine, and Rowen (34). The reason for this is clear if it is recalled that Equation (33) proposed by Wheeler is based on a model wherein a multimolecular gas film builds up on the pore walls until the open section is of sufficiently small diameter for condensation to occur. This is almost certainly the situation when adsorption takes place but it seems highly doubtful that desorption of a full pore occurs in a reverse manner. Therefore, to use other than adsorption data would appear to be at variance with the theory on which the distribution method is based.

After the two experimental inverted isotherms (for the chlorite and KOH-extracted holocellulose) were calculated, it was found that, in both cases, they were best fitted by a curve consisting of the sum of two Maxwellian standard isotherms.[1] When the total volumes under the volume distribution curves had been adjusted to be in the same ratio as the total volumes of nitrogen adsorbed by the

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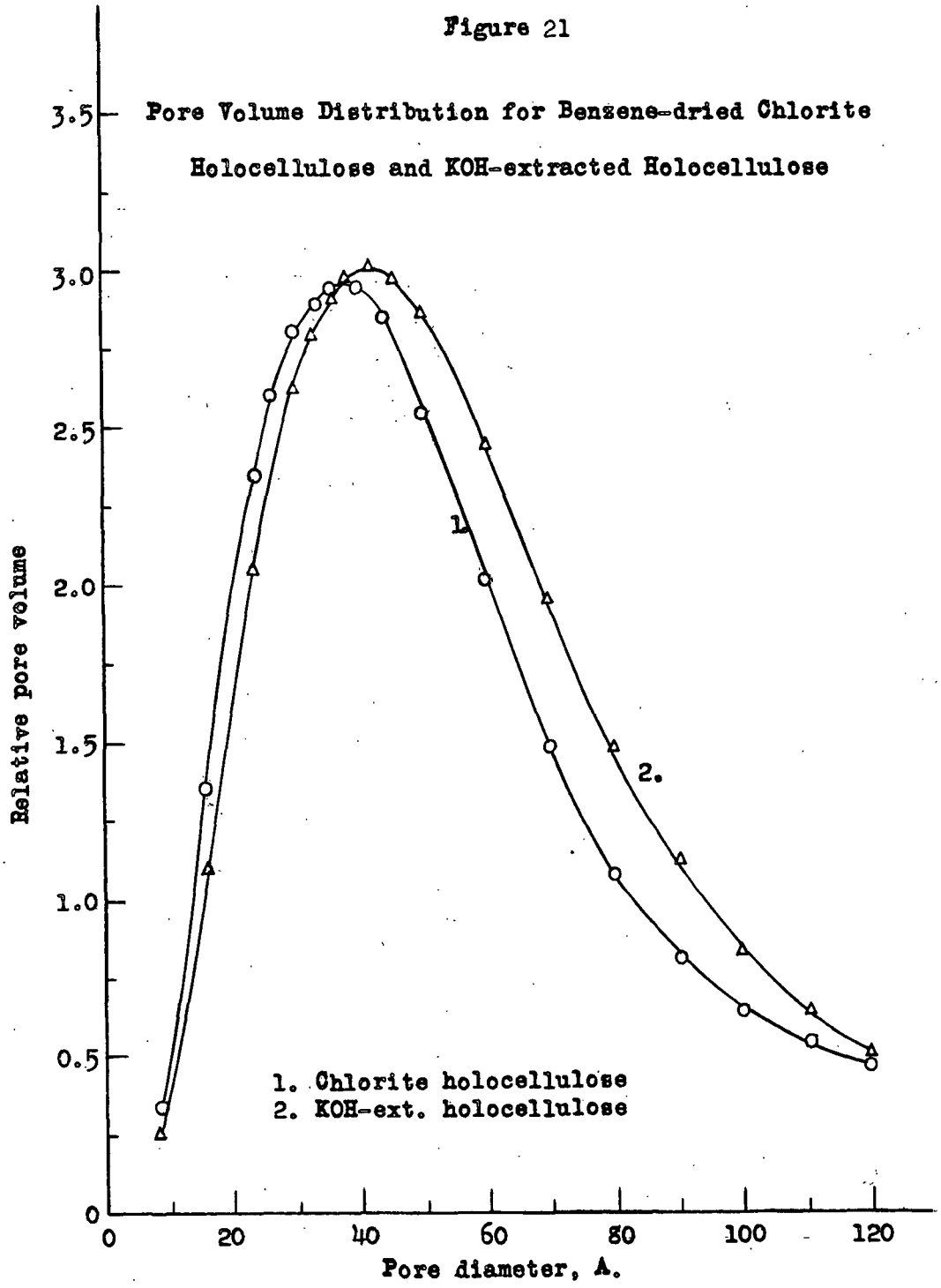
1 The author wishes to acknowledge the consideration shown by Mr. Shull in making available for this work tabulated values for a number of standard inverted isotherms.

KOH-extracted and chlorite holocellulose, the pore volume distributions (see Table R in the Appendix) were plotted against pore diameter in Figure 21. Curve 1 for the chlorite holocellulose indicates that the majority of the accessible submicroscopic spaces in the benzene-dried material have diameters between 10 and 120 A. with the maximum in the volume distribution curve occurring at a diameter of 38 A. After extraction of this chlorite holocellulose with 5% KOH, the resulting material has a pore volume distribution as given by Curve 2. It is noticed that the total volume adsorbed is slightly larger and that the curve has been shifted somewhat toward the higher diameters. The peak in the curve is now at a diameter of 44 A. The alkali treatment either dissolved material containing pores of smaller than average size or removed hemicellulosic materials from the cellulose structure thus enlarging the existing pores to some extent.

The diameters at which the peaks in the volume curves occur for the chlorite and KOH-extracted holocellulose agree fairly well with the diameters of 32 and 40 A. obtained by Hunt, Blaine, and Rowen (34) on water-swollen and caustic-swollen cotton, respectively. Although gas adsorption techniques have provided further information on the subject, the fact that such a system of submicroscopic pores exists between the crystallites and microfibrils of cellulose has been accepted for some time. Frey-Wyssling (79), in discussing the structure of cellulose, states that fibers impregnated with colloidal metals and subjected to x-ray studies have revealed the presence of intercommunicating elongated channels ranging in diameter from 50 to 120 A. In addition, there are also believed to be smaller spaces existing between the micelles which are of the order of 10 A. in cross section. Although the existence of pores with diameters between 10 and 50 A. was not mentioned, it seems reasonable to believe that no sharp diameter demarcation exists but rather

Figure 21

Pore Volume Distribution for Benzene-dried Chlorite Holocellulose and KOH-extracted Holocellulose



that a gradual variation of pore size occurs from those so small as to be of molecular dimentions to channels having diameters considerably in excess of 120 A. Indeed, both the present work and that of Hunt, Blaine, and Rowen previously discussed, indicate that for benzene-dried cellulosic materials the greatest proportion of gas adsorption occurs in pores of this middle range of 20 to 60 A. diameter.

EFFECT OF ABSORBED MOISTURE ON THE ACCESSIBLE AREA OF BENZENE-DRIED, KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Hunt, Blaine, and Rowen (34) have shown that a large part of the internal area of cotton exposed when the wet material is suitably dried from benzene can be closed off by allowing the cotton to absorb water vapor and redrying. This closure of internal area was studied for benzene-dried, KOH-extracted chlorite holocellulose, and it was determined to what extent the original external area of the water-dried material could be approached by exposing a sample of the benzene-dried material to an atmosphere approaching 100% R. H.

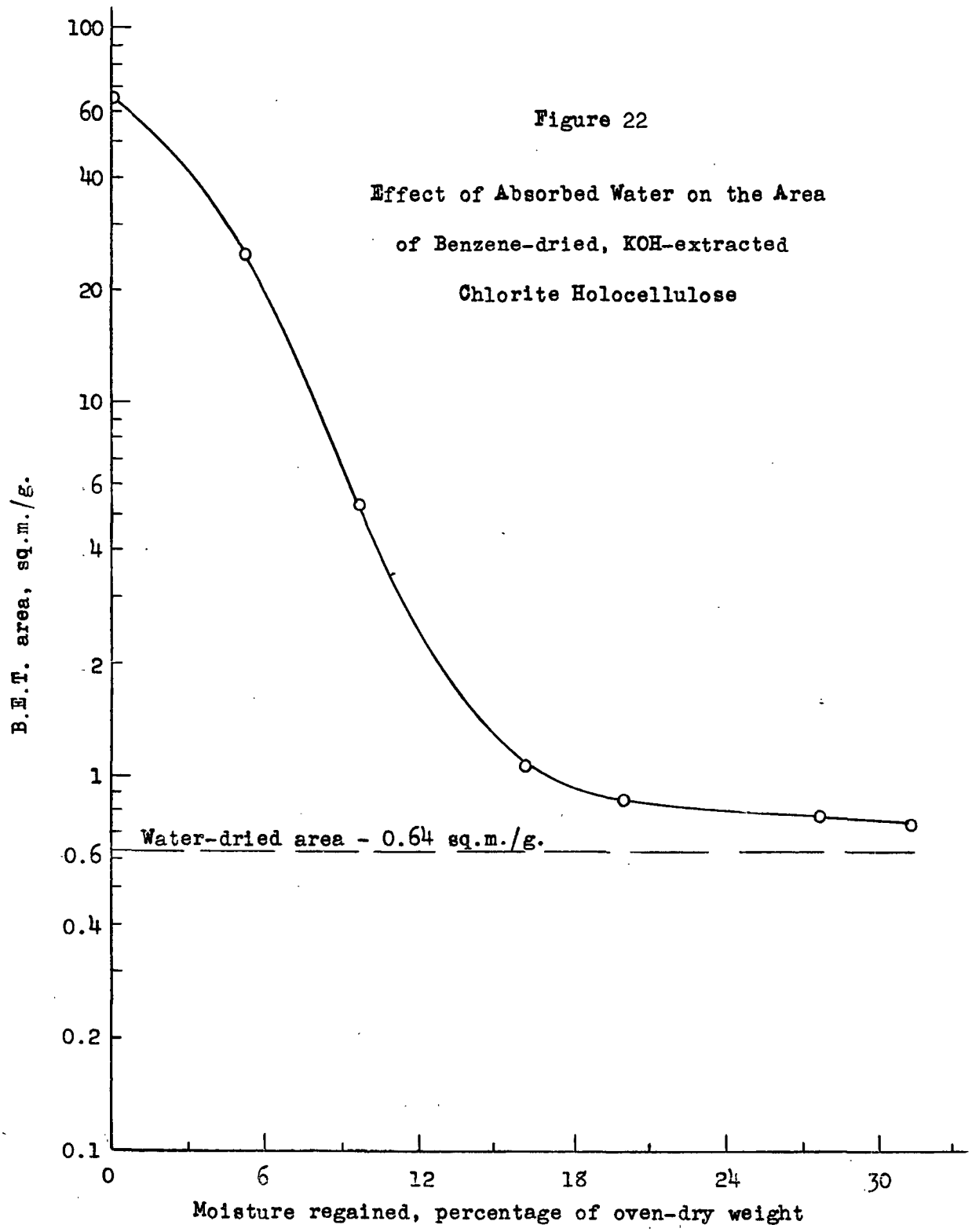
Water-dried, KOH-extracted chlorite holocellulose with a B.E.T. area of 0.64 sq. m. per gram was soaked in water and treated with methanol and benzene to give a material which had an area of 67.0 sq. m. per gram. Samples of this benzene-dried product were allowed to absorb various amounts of moisture by equilibrium exposure to a number of relative humidities between 22.9 and 99.6%. The B.E.T. areas of the exposed and redried specimens are given in Table S in the Appendix. These areas are also plotted on a log scale against the quantity of regained moisture in Figure 22. The original high internal area of the benzene-dried, KOH-extracted chlorite holocellulose was markedly lowered when increasing quantities of water vapor were absorbed and removed. What occurs is thought to be the following. The previous work on this benzene-dried material has shown that it contains a vast number of pores having diameters between 10 and 100 A. When this material is

exposed to water vapor, multilayer adsorption occurs on the walls of these channels even at fairly low relative humidities. Depending upon the size of the pore, after one or more adsorbed layers are built up, the central opening has decreased in radius to the point where capillary condensation of the type predicted by the Kelvin equation takes place. On removal of this adsorbed and condensed water by drying, surface tension forces and hydrogen bonding act to close up and hold shut a majority of those pores which were filled with water.

When the moisture regained has reached about 20% (93% R.H.), the area is only decreased a small amount on further takeup of moisture. Although the original water-dried area was approached, the area of the exposed benzene-dried material is still 20% greater even after absorbing over 30% water. The utmost care was taken during the exposure of the samples to the high relative humidities and it is not likely that the surface of the holocellulose particles ever became wet. Also it seems reasonable that the larger pores were not filled with water even at 99.6% R.H. Therefore, it is probable that the exposed benzene-dried material had area arising from fibrils protruding from the surface and from large pores being open which would be bonded if the exterior of the particles had actually been wet. This would explain the lower area of the water-dried, 40- to 100-mesh material. For benzene-dried, KOH-extracted chlorite holocellulose, then, it was possible to approach but not reach the water-dried unbonded area by equilibrium exposure to a very high relative humidity. This decrease was effected without the occurrence of detectable interparticle bonding. The value of this procedure as a means of estimating the external specific surface of pulp fibers was also investigated as a part of an experiment to be subsequently discussed.

Figure 22

Effect of Absorbed Water on the Area of Benzene-dried, KOH-extracted Chlorite Holocellulose



The work which has been carried out with the KOH-extracted chlorite holocellulose indicates, therefore, that displacement of water from a wet specimen with methanol and drying after displacing the methanol with benzene rendered a very large number of pores of diameter 10 to 120 A. or greater accessible to nitrogen adsorption. However, when the porous benzene-dried material was permitted to absorb sufficient moisture vapor, the initially exposed pores were almost entirely closed.

INVESTIGATION OF THE EXTERNAL SPECIFIC SURFACE AREA OF PULPS AND THE UNBONDED AND BONDED AREAS OF PULP HANDSHEETS

A combination of nitrogen adsorption and the B.E.T. method of area determination has been emplcyed in a detailed consideration of the problem of measuring the dry external specific surface of pulp fibers and the bonded and unbonded areas of paper. With this technique, a study was made of the relationship between the specific scattering coefficient and the unbonded area of water-dried handsheets. Work was also carried out to investigate the differences in unbonded handsheets which had been dried from butanol and from benzene.

Several possible methods were studied to determine which was the most promising for preparing water-dried fibers having a minimum of interfiber bonding. The effect of moisture absorption on the optical scattering and the B.E.T. area of butanol handsheets formed from unbeaten and beaten pulps was investigated. A series of optical and B.E.T. area measurements on "debonded" water-dried fibers, regular and humidified butanol handsheets, and ordinary water-dried handsheets permitted the estimation of bonded area in several different ways. The significance of these values is discussed and the usefulness of optical and gas adsorption techniques for the measurement of bonded area is critically considered.

EXPERIMENTAL PROCEDURES

PREPARATION OF BLEACHED SULFITE PULP

For use in the work on specific surface and bonded area, bleached sulfite pulp was prepared from the same sample of sprucewood employed in the earlier

adsorption studies. A calcium-base cook was carried out in an experimental digester, the pulp was screened and was then bleached in three stages. The conditions used in pulping and bleaching are given in Table X. Bleached pulp having an initial G.E. brightness of 83 was obtained in 45% yield based on the original ovendry wood.

PREPARATION OF BONDED AND UNBONDED HANDSHEETS

Bonded water-dried handsheets were formed in a standard sheet machine employing Institute Method 411 from unbeaten pulp and pulp beaten for various times in a laboratory beater (Institute Method 403). All bonded handsheets were pressed with plates and dried on rings in the usual manner. Handsheets for all beaten pulps were pressed at 50 p.s.i. for 5 and 2 minutes. The handsheets prepared from the unbeaten pulp were also pressed for 5 and 2 minutes but at a number of pressures in addition to 50 p.s.i.

Before the B.E.T. area of these handsheets was measured, each sheet was carefully trimmed to remove the edge which was held in the rings while air drying. All sheets were thoroughly dried in an evacuated desiccator over phosphoric anhydride before sealing in a regular adsorption bulb.

In preparing unbonded pulp sheets by drying from an organic solvent, Parsons (50) and Ratliff (51) actually formed the sheets in butanol. The nonuniformity of formation resulting from this procedure brought about the suggestion by Van den Akker (52) that the sheets be formed in water and that the water then be displaced by successive applications of acetone and butanol. Although this modified procedure was used by Keeney (53) and Leech (54), it has never been described in sufficient detail.

TABLE X

COOKING AND BLEACHING CONDITIONS USED IN PREPARING THE BLEACHED SULFITE PULP

Cooking	
Liquor ratio	5 to 1
Total SO_2, g./100 ml.	6.04
Combined SO_2, g./100 ml.	1.28
Cooking schedule, hr.	
Up to 110°C.	3
110 to 140°C.	3
At 140°C.	2.8
Total cooking time	9
Maximum pressure, p.s.i.	85
Bleaching	
Chlorination	
Consistency, %	3
Temperature, °C.	22
Chlorine added, %	4
Time of treatment, hr.	1
Caustic extraction	
Consistency, %	10
Temperature, °C.	40
NaOH added, %	1
Time of extraction, hr.	1
Calcium hypochlorite	
Consistency, %	5
Temperature, °C.	38
Hypochlorite added, %	0.75
Time of treatment, hr.	4
pH	above 8

The procedure as it was employed in the present work is as follows: The pulp was stirred for 10 minutes (if unbeaten), the stock was diluted, and hand-sheets were formed in the sheet machine following Institute Method 403. However, to assist in the subsequent solvent treatment, the drainage valve was shut just after the free water had drained from the sheet so that the hydraulic leg was maintained below the wire. The sheet mold was opened and a sheet of Whatman No. 1 filter paper having a diameter of 18.5 cm. was carefully placed over the wet sheet and the mold closed. Approximately 500 ml. of acetone were gently poured down the side of the mold and allowed to permeate through the filter paper and the pulp sheet over a period of about 5 minutes. This operation was repeated twice more with 500 ml. of acetone to thoroughly displace the water. Removal of the acetone was effected by the successive application of three 500 ml.- portions of either butanol or benzene again allowing 5 minutes for each treatment. The sheet mold was opened, a blotter was placed over the sheet, and after lightly pressing, the solvent-wet sheet was carefully removed from the wire. A second blotter was placed in contact with the wire side of the sheet. Following 7 minutes pressing at 50 p.s.i., the sheet still between blotters was placed in rings until dry and conditioned at 73°F. and 50% R.H.

INVESTIGATION OF VARIOUS POSSIBLE METHODS OF OBTAINING WATER-DRIED UNBONDED FIBERS

Several different techniques were investigated with the object of finding a way to obtain water-dried pulp fibers which have a minimum of fiber-to-fiber bonding. Each method which was studied will be outlined and briefly discussed.

Sand Drying-Air Elutriation Method

It was thought that it might be possible to separate wet pulp fibers with some

material such as sand so as to minimize fiber-to-fiber contact and hence bonding when drying was taking place. Then when the mixture was dry, separation of the fibers from the sand particles would be accomplished by air elutriation.

Quartz sea sand (20- to 40-mesh) was cleaned and exposed to the vapors of dimethydichlorosilane (DC 1208). In this way, each particle was covered with a thin water-repellent film to prevent bonding of the fibers to the sand. Sufficient dry, treated sand was added with vigorous stirring to a quantity of 0.1% consistency pulp until the resulting slurry would just circulate. The mixture was quickly filtered and dried at 105°C. A portion of the dry sand and fiber was maintained in a fluidized state in an elutriation column in the attempt to remove the fibers. However, the boiling action of the bed tended to form some of the pulp fibers into clumps or balls which were soon too dense to pass over in the air stream. Also the movement of the dry fiber and sand within the glass cylinder imparted to each a static charge which caused both fibers and sand particles to adhere to the walls of the column. Attempts to dissipate or prevent this charging were not successful. Because of these two phenomena, little fiber passed out of the column and it was concluded that this method was not satisfactory for the preparation of unbonded fibers.

High-Temperature Spray-Drying Method

In connection with past project work done by the pulping section of the Institute, a small-scale, spray-drying apparatus was constructed. Although the original purpose of this equipment was for the preparation of finely powdered salts from their solutions, its utility for preparing dry unbonded pulp fibers was investigated. Little difficulty was experienced in feeding the stock with a

Sigmamotor tubing pump through the fine tube of the spray nozzle or in maintaining the apparatus in continuous operation. The dried material which was collected, however, was in the form of small, rather compact flakes or balls which seemed to have appreciable bonding between fibers. Variation of the operating conditions did little to alter the appearance of the product. It was thought that this agglomerated condition may have been caused both by the flocculation of fibers in the feed tube to the spray nozzle and by the rolling action of the tangential blast of drying air. The method was not employed further.

Room-Temperature Spray-Drying Method

Additional work using the principle of spray drying was undertaken by investigating the possibility of spraying a dilute pulp slurry over a large area so that the contact and hence the bonding between fibers is minimized when drying. The actual procedure employed involved first spraying a 0.20 to 0.25% consistency pulp slurry (distilled water) onto a 5 by 11 ft. horizontal sheet of polythene with a hand spray gun. The spraying was carried out so that the surface of the sheet was covered with a fine mist and approximately 0.8 g. of oven-dry fiber were spread over 55 sq. ft. A wooden frame covered with a paper tarpaulin was supported just above the sprayed sheet to prevent contamination by dust, and the fibers were allowed to dry at room temperature. When drying was complete, the fibers were gently brushed from the polythene with a lint-free cloth and removed with a vacuum collector. The vacuum system consisted of a flattened glass suction nozzle connected through a fiber collector to a hand vacuum cleaner. The collector was constructed by connecting two 5 in. glass funnels to a 5 in. diameter round board container which had a large filter paper taped over one end. This device

effectively collected the dry pulp fibers removed from the polythene by the suction.

A preliminary experiment was carried out to determine if this method of drying the pulp fibers appeared to entail any loss of fines or contamination by dust. This consisted of first determining the silvered area by the Clark method (45, 46) of a sample of unbeaten bleached sulfite pulp which had never been dried below a moisture content of 75%. A portion of this same pulp was filtered on a Büchner funnel and air dried at room temperature. Another portion was spray dried in the manner just discussed. Both of the dried materials were soaked in water overnight and then gently defibered. Silvered areas measured on all three samples are given in Table XI.

TABLE XI

SILVERED AREAS OF UNDRIED AND DRIED UNBEATEN BLEACHED SULFITE PULP

History of Pulp Fibers	Silvered Area, sq. m. / g.
Undried	1.22
Filtered and dried as a pad	0.98
Spray-dried on polythene	1.02

The values of silvered area for the spray-dried fiber and for the pulp dried after filtration do not indicate that any loss of fines or that any appreciable contamination of the spray-dried material occurred. However, it is interesting that the silvered areas of the samples which have been dried and resoaked are approximately 20% lower than the area of the undried sample. It is very possible that a certain amount of irreversible shrinkage occurs during the initial drying which is responsible for the lower observed silvered areas. Of the methods which have been investigated as possible means of securing dry fibers with a minimum of

interfiber bonding, this room-temperature, spray-drying technique appears to be the most satisfactory. However, only after the method has actually been tried can it be determined whether it will permit fibers suitable for specific surface studies to be obtained from beaten and unbeaten pulps. Therefore, the usefulness of this spray-drying method is considered further in the subsequently reported work on bonded area.

METHODS EMPLOYED FOR THE ESTIMATION OF BONDED AREA

An estimation of the bonded area of regular handsheets formed from unbeaten and beaten bleached spruce sulfite pulps has been made following four different procedures.

Optical Method

The bonded area of the handsheets was initially determined by the regular optical method. Since this technique has been discussed in detail by Ratliff (51), it will only be outlined briefly at the present time. Water-dried sheets were formed from the unbeaten sulfite pulp and pulp refined for 5, 12, and 24 minutes in a laboratory beater in the manner previously discussed. Butanol handsheets were also prepared from the same pulps. Portions of each pulp were formed into sheets in the sheet mold but without pressing or drying were used to determine the silvered area following the procedure described by Browning (48). Both the water-dried and butanol-dried sheets were dried and conditioned at 73°F. and 50% R.H., and two measurements of the specific scattering coefficient were made on five sheets of each type at 600 mmu using the General Electric Recording Spectrophotometer. Values of R_o (single sheet backed by black velour paper) and R_∞ (single

sheet backed by an optically infinite pad of similar sheets) were determined by correcting the respective values measured relative to a magnesium carbonate standard whose absolute reflectance at this wavelength was 0.98. Using the Bureau of Standards opacity charts (80), the values of the scattering coefficients corresponding to R_0 and $R\infty$ were determined. These were converted to the specific scattering coefficients by dividing by the basis weight expressed in grams per square centimeter. The average value of the coefficient for the water-dried sheets was divided by that for the butanol sheets and the ratio was multiplied by the silvered area to give an estimate of the unbonded area of the regular handsheets. When this unbonded area was subtracted from the silvered area, an estimate was obtained of the bonded area of the water-dried sheets.

Humidification-Optical Method

It was felt that the equilibrium exposure of the unbonded butanol sheets to a high relative humidity and redrying might cause a decrease in the specific scattering coefficients of the sheets through the closure of accessible internal pores. Since, if such a decrease takes place, it would be due to intrafiber and not interfiber bonding, such exposure may permit a more accurate bonded area to be determined by the optical method.

Butanol pulp sheets which were used for the regular optical method were placed in a desiccator over a saturated solution of sodium fluoride (96.7% R.H.), and the desiccator in turn was placed in an insulated cabinet at 73°F. Small portions of each set of sheets were placed in separate dish units of the type described by Wink (75) which contained saturated solutions of the same salt. These dishes were also kept in the insulated box and the specimens were periodically weighed to

determine when equilibrium absorption of moisture was reached. Approximately three weeks were required for the sheets to acquire a total moisture content of 23.5 to 25.0%. After drying and conditioning at 73°F. and 50% R.H., the specific scattering coefficients of the sheets were measured and these values were employed for the computation of bonded area by the optical method.

Humidification-B.E.T. Area Method

From the study which was made of the closure of the accessible internal area of benzene-dried, KOH-extracted chlorite holocellulose by absorbed water vapor, the idea arose of the possible use of the nitrogen adsorption-B.E.T. area of the butanol sheets exposed to a high relative humidity as an estimate of the external specific surface area of the pulp. Since the water-dried area of the KOH-extracted chlorite holocellulose was not reattained when a benzene-dried sample was allowed to absorb over 30% moisture and was redried, it is not likely that the closure of the internal area of the butanol sheets will be complete. Nevertheless, the difference in the B.E.T. areas measured on the exposed unbonded butanol sheets and on water-dried handsheets will provide a measure of what can be termed the "maximum" bonded area. In other words, when the area of the moisture-exposed butanol sheets is measured by gas adsorption, all of the external specific surface of the dry pulp is being determined and, in addition, an indeterminate portion of the internal area. Therefore, the estimate of the specific surface area of the pulp can only be in error on the high side. The measurements of bonded area made using this specific surface will be equal to or larger than the true bonded area and, hence, can be taken as a "maximum" value.

After the exposed butanol sheets of the beaten pulps had been employed for the measurement of the specific scattering coefficients discussed in the previous section, they were dried, were sealed in adsorption bulbs, and the B.E.T. area was determined. The resulting areas were taken as the specific surface of the unbonded dry pulps and they were used in conjunction with nitrogen adsorption areas measured on the respective water-dried handsheets for the estimation of bonded area.

Spray Drying-B.E.T. Area Method

The final method employed for an estimation of bonded area made use of the room-temperature, spray-drying technique which has already been discussed in detail. The procedure followed for each pulp was to first form approximately twenty handsheets in the sheet mold. Since some fines are lost through the wire, this step was included so that the pulp to be spray dried would have also undergone the drainage operation. The sheets were not pressed or dried, however, but were slurried in distilled water and spray dried on polythene. This spraying and drying operation was repeated until approximately 10 g. of dry fiber were obtained for the unbeaten pulp and the pulps beaten for 5, 12, and 24 minutes. Measurements of optical scattering and of the nitrogen adsorption area were made on samples of each of these dried pulps.

In order to measure the specific scattering coefficients of the spray-dried fibers, it was necessary to first form them into sheets having a fairly even formation. To accomplish this, an apparatus was constructed which could be used to form air-laid pulp sheets. This device consisted of a 2 in. glass column about 20 in. high which was fitted at the bottom with an air inlet and a propeller driven

by an air stirrer. A curved piece of 1 in. glass tubing led from the top of the column to a short vertical 2 in. tube which was sealed at the lower end by a filter paper. In operation, a quantity of spray-dried fiber was added to the column, the air stirrer turned on, and the air stream regulated so that individual fibers knocked loose by the rotating propeller were blown up and out of the column. These fibers were caught and were formed into thin pulp sheets on the horizontal filter paper.

As each sheet was prepared, it was pressed at 50 p.s.i., was removed from the filter paper, and was immediately placed between two tared Ethocel sheets for protection while weighing and handling. For measurement of the scattering properties, the top piece of Ethocel was removed, and a cup lined with black velvet (used as a black body) was pressed against the sheet. When the cup was raised, the air-laid sheet adhered to the rim of the cup and in this position the value of R_o was determined. To determine R_∞, the sheet was pressed against the optically infinite pad to which it adhered, permitting the cup to be removed.

It will be seen in the following section that the values of the specific scattering coefficients for the air-laid pulp sheets were low and somewhat inconsistent. Because of this, an estimation of bonded area was not made from the data obtained. The possible reasons for these anomalous scattering values will be discussed when the results are presented.

The area of each of the spray-dried pulps was measured using nitrogen adsorption measurements. If fines are not lost in handling and if bonding between fibers and fiber fragments has been essentially eliminated by means of the spray-drying technique, the difference between the B.E.T. areas of the water-dried unbonded

fibers and the water-dried handsheets formed from the same pulp represents the numerical bonded area of the handsheets. In actual practice, however, it is quite possible that some fines are lost because of the extremely light and fluffy nature of the spray-dried fibers. Also, it is reasonable to believe that whereas the bonding between fibers has been minimized by the spray drying procedure, it has not been completely eliminated at least for pulps which have been beaten. Because of these reasons, the specific surface of the spray-dried pulps as measured by gas adsorption, when in error, will be lower than the true external surface area of the dried fibers. It follows directly then that the actual bonded area of the handsheets must be equal to or higher than the bonded area values determined in this way. Therefore, the area obtained from the difference in the B.E.T. area of the spray-dried pulp and the corresponding area of the water-dried handsheets represents a "minimum" bonded area. Calculation of these "minimum" values of bonded area was made for the handsheets formed from the unbeaten and each of the beaten pulps.

EXPERIMENTAL RESULTS AND DISCUSSION

RELATIONSHIP BETWEEN THE SPECIFIC SCATTERING COEFFICIENT AND THE B.E.T. AREA OF BLEACHED SULFITE HANDSHEETS

One of the basic assumptions in applying the optical method of measuring the bonded area of paper is that all of the original external surface area of the fibers in the sheet which does not scatter light is involved in interfiber bonding. If, as is most probable, it is largely hydrogen bonding which takes place between pulp fibers, then those portions of each fiber actually bonded are known to be separated by distances of 2 to 3 A. (73). Since light scattering is not thought to take place unless two surfaces are separated by at least 400 to 500 A., there has been some question as to the strict reliability of employing the specific scattering

coefficient for the measurement of bonded area. A nitrogen molecule, on the other hand, has an approximate diameter of 4.3 A. (37), and it is quite reasonable to believe that nitrogen adsorption does not take place on that area involved in fiber-to-fiber bonding. Because of this small size of the nitrogen molecules, it is felt, however, that the area measured by gas adsorption is very close to the actual unbonded area of a sheet of paper. To test the validity of using the specific scattering coefficient as a measure of relative unbonded area, the unbonded area of various water-dried handsheets was determined and these values were compared with the specific scattering coefficients measured on the same sheets.

For this work, handsheets having various bonded areas were desired. The bonded area of the sheets which were used was altered in one of two ways: (1) by a variation in the degree of wet pressing of unbeaten pulp sheets or (2) by refining the pulp from which the handsheets were formed. In the wet pressing experiment, unbeaten, bleached sulfite pulp with a Schopper-Riegler freeness of 865 cc. was first formed into handsheets in the sheet mold. Approximately 120 sheets were prepared and sets of twenty of these were pressed at 1, 10, 50, 150, 400, and 4000 p.s.i. Standard handsheets were also prepared from pulp which was unbeaten and which had been refined in a laboratory beater for 5, 12, and 24 minutes to give stock which had a Schopper-Riegler freeness of 830, 755, and 500 cc., respectively.

The specific scattering coefficient and the B.E.T. area of each set of sheets were determined. In addition, the tensile strength (15 mm. strips with 2.93 in. between clamps) was measured following Institute Method 511. The tensile values were converted to pounds per inch at a basis weight of 46 lb. (25 x 40 - 500). These data for the various handsheets are given in Table XII. Also, the B.E.T. area is plotted against the specific scattering coefficient for each set of sheets in Figure 23.

TABLE XII

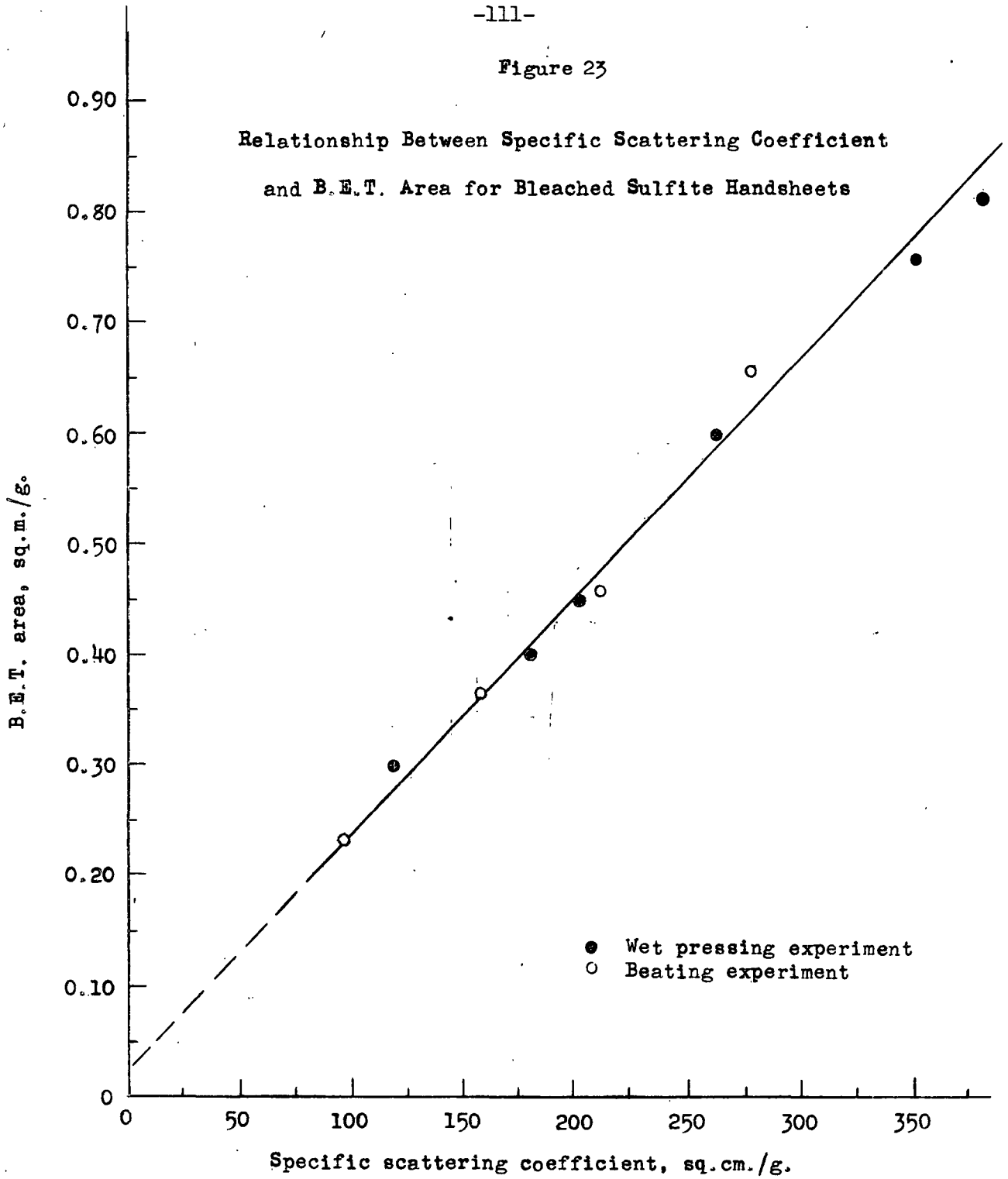
PROPERTIES OF HANDSHEETS FORMED FROM UNBEATEN AND BEATEN BLEACHED SULFITE PULP

	S.-R. Freeness of Pulp, cc.	Wet Pressure, p.s.i.	Specific Scattering Coefficient sq. cm./g.	B.E.T. Area, sq. m./g.	Schopper Tensile lb./in. (at 46 lb. per ream)
Wet pressing experiment					
	865	1	379	0.81	5.5
	"	10	352	0.76	10.8
	"	50	268	0.60	17.3
	"	150	204	0.45	21.0
	"	400	181	0.40	22.0
	"	4000	118	0.30	24.0
Beating experiment					
	865	50	278	0.66	15.4
	830	"	213	0.46	26.6
	755	"	160	0.37	28.5
	500	"	98	0.23	30.7

It is noted in Figure 23 that a good linear relationship exists between the gas adsorption area and the scattering properties of the sheets. This correlation serves to confirm the belief that the specific scattering coefficient of a water-dried handsheet is directly related to the unbonded area regardless of whether this area was arrived at by beating or by wet pressing. When the straight line plot is extrapolated to lower scattering and area values, it is seen that it does not pass through the origin. With regard to this, it is interesting to note that the minimum B.E.T. area of a handsheet made in a standard sheet machine is 400 sq. cm. (the total area of both external surfaces of the sheet). An ordinary handsheet

Figure 23

Relationship Between Specific Scattering Coefficient and B.E.T. Area for Bleached Sulfite Handsheets



of this size has a basis weight of about 0.0065 g. per sq. cm. From Fresnel's law, it has been shown that for a sheet of glass having an index of refraction close to that of cellulose, a total of approximately 8% reflection occurs at the two air-glass surfaces when the light is at normal incidence (81). The Kubelka-Munk theory (82) is such that for specimens having a very low scattering power, R_o is essentially equal to the scattering power. Therefore, the minimum value of the specific scattering coefficient of a regular handsheet can be estimated by dividing 0.08 by 0.0065 to give 12 sq. cm. per gram. If a point were plotted in Figure 23 at a B.E.T. area of 0.04 sq. m. per gram and a specific scattering coefficient of 12 sq. cm./g., it would fall almost on the extrapolated plot. It appears, therefore, that the slope of the linear relationship obtained in Figure 23 is reasonable and that when extended the plot should not be expected to pass through the origin.

The measurements of nitrogen adsorption area carried out as a part of this work represent the first detailed study which has been made of the numerical unbonded area of a series of handsheets without the necessity of employing a silvering area measured on water-swollen pulp. If wet pressure is used as the sole means of altering the bonded area of the sheets so that the specific surface area of the pulp remains unchanged, gas adsorption techniques will permit the actual change in bonded area to be measured in, for example, square meters per gram. Also, if the bonded area change is to be measured on a number of pressed sheets of the same beaten or unbeaten pulp, the B.E.T. area and the specific scattering coefficient could be measured on several of the sheets to calibrate the linear relationship between the two. The more rapid optical method will then permit numerical values of the bonded area change to be determined with a minimum of work. The technique which has just been discussed does not provide a means for measuring the actual

bonded area of a pressed sheet, but only the change in this area. Furthermore, it cannot be employed to measure even the changes in the bonded area brought about by beating since the specific surface area of the pulp is altered on refining. Finally, it should be stressed that this work has only demonstrated the validity of one of the several assumptions made in applying the optical method for the measurement of bonded area. The experiment has shown that the relative unbonded area of water-dried handsheets can be quickly and easily obtained from optical scattering measurements.

COMPARISON OF BUTANOL AND BENZENE HANDSHEETS OF UNBEATEN SULFITE PULP

In the optical method of determining bonded area, the difference in the specific scattering coefficient of a water-dried handsheet and of an unbonded sheet dried from a nonswelling organic solvent is taken to be proportional to the fiber-to-fiber bonding in the bonded sheet. Parsons (50) used n-butyl alcohol (butanol) to form unbonded sheets after the water was displaced from the wet fibers with acetone and the acetone was displaced with butanol. Parson's choice of butanol, although apparently somewhat arbitrary, was based on the findings of Kress and Bialkowsky (83) that the swelling of unbleached Mitscherlich pulp by butanol was less than 5% of that produced by water. Ratliff (51) also employed butanol for the preparation of unbonded pulp sheets. Keeney (53) stated that in a preliminary experiment in which slash pine semichemical kraft pulp was dried from both butanol and benzene the specific scattering coefficients were approximately equal. However, because of other considerations, namely, that butanol has a dipole moment whereas benzene does not and that white pine does not swell in benzene whereas in butanol the relative volumetric swelling is 13.5% of that for water, benzene was substituted for butanol. Following the lead of Keeney, Leech (54) also employed benzene.

Because butanol has never been shown to be unsatisfactory for preparing unbonded handsheets and because no data have been given to indicate that benzene is superior for this purpose, it was felt that a study of the relative applicability of the two organic solvents should be undertaken before concluding which is the more suitable. Therefore, a number of unbonded handsheets were prepared from unbeaten bleached sulfite pulp, half of which were dried from butanol and half were dried from benzene following the procedure previously discussed. The specific scattering coefficient of each set of sheets was determined. One butanol and one benzene sheet were dried, sealed in separate adsorption bulbs, and their B.E.T. area determined. The remaining sheets were exposed to 96.7% R.H. in the manner already outlined. Approximately three weeks were required for the butanol and benzene sheets to equilibrate at a moisture content of 24.3 and 24.2%, respectively, based on the original ovendry sample. The exposed sheets were dried at 73°F. and 50% R.H., and their specific scattering coefficients and nitrogen adsorption areas were measured. The results of this experiment are given in Table XIII.

TABLE XIII

OPTICAL AND AREA MEASUREMENTS ON BENZENE AND BUTANOL SHEETS OF UNBEATEN BLEACHED SULFITE PULP

	Butanol Sheets	Benzene Sheets
Specific scattering coefficient, sq. cm./g.		
Originally	565	634
After equilibrium exposure to 96.7% R.H.	543	600
B.E.T. area, sq. m./g.		
Originally	4.18	10.8
After equilibrium exposure to 96.7% R.H.	2.34	3.68

It was originally thought that the absorption of large quantities of moisture vapor by the two sets of sheets might considerably reduce or eliminate the difference in the specific scattering coefficients but this did not take place. Rather, it is seen that both before and after exposure to a high relative humidity the specific scattering coefficient of the benzene sheets is approximately 10% greater than for the sheets dried from butanol. Also the area of the sheets as determined by nitrogen adsorption is considerably greater in both cases for the benzene sheets than for the butanol sheets. When the handsheets were allowed to absorb approximately 24% moisture vapor and were redried, both the specific scattering coefficient and the gas adsorption area decreased although in the former case the change was small. The reason for this relatively large change in the B.E.T. area in comparison to the specific scattering coefficient can be quite logically explained if the previously discussed work with the benzene-dried chlorite holocellulose is reviewed. It was demonstrated that the accessible internal pores in this material were mainly between 10 and 120 A. in diameter and that these pores were almost entirely closed by drying after exposure to a high relative humidity. It is reasonable to believe that the exposed pores in the benzene-dried and butanol-dried pulp specimens are of similar diameter. It should be remembered, however, that pores of this diameter are probably of too small a size to influence the scattering properties of the fibers whether they are open or closed. Therefore, whereas the B.E.T. areas of the benzene and butanol sheets are considerably decreased when large amounts of absorbed moisture are removed, the specific scattering coefficients are not appreciably altered.

For the unbeaten pulp being studied, there is little doubt that a difference in properties exists between the butanol and benzene handsheets. The strength of

both types of sheets is very low and it does not appear that differences in fiber-to-fiber bonding can be responsible for the differences which are noted in the gas adsorption area and the light scattering. These differences more likely arise from the fact that butanol has a small swelling effect on pulp whereas benzene has none. Therefore, when fibers are dried from butanol they will shrink slightly more and become somewhat less porous than when dried from benzene. The slightly greater external area and porosity of the benzene-dried fibers would explain the greater B.E.T. area and the higher specific scattering coefficient which has been observed. Since the bonded area is apparently negligible in either case, it would appear that the difference in the specific scattering coefficients of the benzene and butanol sheets indicates a difference in bonding which does not actually exist. The values of bonded area as measured by the optical method will, therefore, be spuriously high when benzene is used. It would appear that, of the two solvents, butanol is more suitable than benzene for the preparation of unbonded handsheets.

AREA STUDIES ON BLEACHED SULFITE PULPS AND HANDSHEETS

Since the optical method developed by Parsons (50) is the only convenient means available for the estimation of the bonded area of paper, it has been employed to a considerable extent in the past few years. The method has been criticized by Mason (84), however, who states that in drying the unbonded fibers from butanol with its low swelling action, the fiber shrinkage is probably considerably less than in drying from water. Thus one might expect the butanol-dried fibers to have a higher area and hence a somewhat higher specific scattering coefficient than if the same fibers had been dried from water has been demonstrated by the recent work of Leech (54). He prepared small quantities of unbonded water-dried fibers by filtering a very dilute suspension of a fractionated beaten pulp on a dyed filter paper and

removing the individual fibers with forceps after drying. Separated fibers, from which the water had been displaced by successive applications of acetone and benzene, were prepared in the same way. Portions of both the benzene-dried and water-dried unbonded fibers were formed into small pads and the specific scattering coefficients were determined. Leech found that the value of the coefficient obtained for water-dried unbonded fibers was only 59% of that for the benzene-dried unbonded fibers. In light of these results, it appears that it may not be justifiable to attribute the difference in the light-scattering properties of a butanol-dried sheet and a water-dried sheet solely to differences in bonded area. Since this is one of the main assumptions of the optical method of measuring bonded area, it is seen that the validity of the method can be questioned.

An investigation was carried out of the optical method and of the other methods of estimating the bonded area of handsheets already discussed. The requisite estimates of external specific surface area are critically considered and the values of bonded area obtained by each method are discussed with regard to the nature of the procedure which was employed and in connection with the values obtained by the other methods.

Optical Properties of the Various Pulps and Handsheets

Values of the silvered areas of the pulps and of the specific scattering coefficients for the unbeaten and beaten pulps and handsheets are given in Table XIV. The unbonded and bonded areas of the water-dried handsheets computed from these data are also included. It is noted from the table that both the silvered areas of the pulps and the specific scattering coefficients of the butanol handsheets increase in the normal fashion as beating progresses. Likewise, the specific

scattering coefficients of the water-dried handsheets decrease regularly as the pulp from which they were formed was refined to a greater degree. Similar scattering measurements on the air-laid sheets of the spray-dried pulps, however, not only do not increase in the expected manner but are lower for the beaten than for the unbeaten pulp. In addition, the value for an unbeaten air-laid sheet is lower than that which was measured for a water-dried unbeaten pulp sheet pressed at 1 p.s.i. indicating that it too is somewhat in error.

These low and irregular values of the specific scattering coefficients of the spray-dried pulps could be due to a number of reasons. In fact, almost anything which might occur during the procedure of spray drying, sheet forming, and handling, i.e., bonding between fibers, loss of fines, discoloration or contamination of the pulp, or nonuniform formation of the air-laid sheets, tends to depress the scattering value. Because of its nature, the unbeaten pulp contains few fines and when spray-dried is thought to have very little bonding between fibers. Therefore, the low specific scattering coefficient obtained would appear to be most probably caused by a discoloration of the fiber or by irregular formation of the air-laid sheets. Despite the care taken in forming the air-laid sheets from the spray-dried fiber, these could not be obtained with as regular a formation as for the water-fromed sheets, therefore, formation considerations are no doubt involved. A check of G.E. brightness, however, showed that it was decreased from 3 to 4 points by the spray-drying operation. It is felt that this decrease in brightness contributes to the greater extent to the depressed scattering values of the unbeaten pulp. Discoloration of the fiber during drying is thought to be due mainly to dust removed from the air as the slurry was sprayed or settling on the pulp in spite of the protecting tarpaulin as it was drying. It is probable that a small

TABLE XIV

OPTICAL PROPERTIES OF PULPS AND HANDSHEETS

	Beating Time, min.			
	0	5	12	24
S.-R. freeness, cc.	865	830	755	500
Silvered area, sq. m./g. A	1.26	1.64	2.13	2.57
Specific scattering coefficient, sq. cm./g.				
Water-dried sheets B	278	213	160	98
Air-laid pulp sheets	303	262	256	289
Butanol-dried sheets				
Originally C	565	578	637	752
After exposure to 96.7% R.H. D	543	574	635	751
Surface area, sq. m./g.				
Original butanol sheets				
Unbonded (from A,B, and C) F	0.62	0.60	0.54	0.33
Bonded (A-F)	0.64	1.04	1.59	2.24
Exposed butanol sheets				
Unbonded (from A,B, and D) G	0.65	0.61	0.54	0.33
Bonded (A-G)	0.61	1.03	1.59	2.24

amount of dust adhering to the wet fibers would do little to change the fiber area when dry, but that it would have an effect on brightness and other optical properties. Any dust picked up during the recovery of the dry fiber from the polythene sheet would also discolor the pulp and, in addition, would affect the gas area to some extent.

Discoloration and formation difficulties will, of course, also influence the specific scattering coefficients measured on the spray-dried beaten pulps. The observed results indicate, however, that increased bonding between the fibers and fibrils of the spray-dried pulps may be taking place as beating progresses. Also, as more fines are produced by refining, the liklihood of these being lost when the dry fibers are handled is increased. The conclusion was reached that the use of air-laid sheets produced from spray-dried pulps in the manner discussed was not a satisfactory technique for determining the true specific scattering coefficient of the unbonded pulp fibers. These scattering values were not employed further. However, the spray-drying technique will be discussed in the following section with regard to its usefulness as a means of preparing dry fiber for area measurements by nitrogen adsorption.

It will be recalled that the specific scattering coefficient of the unbeaten butanol sheets originally reported in Table XIII and also included in Table XIV, was only slightly decreased on equilibrium exposure of the sheets to 96.7% R.H. and redrying. It is seen in Table XIV that when a similar takeup of moisture occurred for the butanol sheets formed from beaten pulps, the observed decrease in scattering was even less. As was previously discussed, the probable reason for this behavior is that the absorbed moisture mainly affected submicroscopic internal pores and channels of a diameter considerably smaller than that necessary to scatter light.

Employing the specific scattering coefficients of the water-dried and butanol-dried handsheets and the silvering areas of the pulps, the unbonded and bonded areas of the regular handsheets were determined by the optical method and are given in Table XIV. Similarily, the specific scattering coefficients of the exposed butanol sheets were used to determine values of bonded area by the optical method. In all instances, the areas were almost or actually identical. Therefore, it was concluded from these results that permitting the butanol sheets to absorb large quantities of moisture and redrying before making the scattering measurements does little to alter the optical method as a measure of bonded area.

B.E.T. Area Measurements on Pulps and Handsheets

Values of the accessible surface area of the spray-dried pulps, the water-dried handsheets, and the butanol handsheets after equilibrium exposure to 96.7% R.H. as determined by nitrogen adsorption and the B.E.T. method (molecular area, 16.2 sq. A) are given in Table XV. The unbonded area of the water-dried handsheets decreased in the expected manner as the pulp was beaten. The B.E.T. area of the spray-dried pulp and of the exposed butanol handsheets both show little change until the pulp has been beaten to a considerable extent. It is not believed, however, that this similarity in behavior is due to the same factors.

TABLE XV

B.E.T. AREA MEASUREMENTS ON PULPS AND HANDSHEETS

	Beating Time, min.			
	0	5	12	24
B.E.T. area, sq. m./g.				
Water-dried sheets A	0.66	0.46	0.37	0.23
Butanol sheets after exposure to 96.7% R.H. B	2.34	2.31	2.33	2.75
Spray-dried pulp C	0.81	0.78	0.82	1.05
Bonded area, sq. m./g.				
"Maximum" (From A and B)	1.68	1.85	1.96	2.52
"Minimum" (From A and C)	0.15	0.32	0.45	0.82

The manner in which the area of the exposed butanol sheets changes as the pulp is refined suggests that the beating action which increases the specific surface of the pulp also conditions the gross internal structure in such a way that it is more readily closed when the sheets absorb moisture. Only when the beating has progressed for some time does the creation of external surface overshadow the increased ability of the pores to close on moisture takeup, and the B.E.T. area of the exposed butanol sheets increases. Since the high areas obtained are obviously a combination of external and internal area, these values are of little use except as a means of determining the "maximum" bonded area already discussed.

With regard to the spray-dried pulps, it should be noted that in each instance the areas are considerably lower than the silvering areas of the corresponding materials. Also, whereas the silvered areas increased regularly as the pulp was refined, the B.E.T. areas of the spray-dried fibers did not. In order to explain this irregular behavior of the dry fiber area on beating, it is necessary to consider once again the nature of the method by which the fibers were dried. The technique involved spreading the fibers out over a large area while they were drying so

that contact and hence interfiber bonding were minimized. As will be subsequently discussed, the unbeaten pulp, consisting as it does largely of whole fibers, is probably relatively unbonded in the spray-dried state. As the pulp is beaten, fibers are cut and broken, and fibrils are split off the parent fiber. When this happens it apparently becomes increasingly difficult, if not impossible, to prevent fiber-to-fiber bonding even though a small quantity of pulp is spread over a very large area to dry. With full cognizance of the fact that for beaten fibers some bonding has occurred, a measurement of the area of the spray-dried pulps still permits an interesting measure of "minimum" bonded area.

These estimates of "maximum" and "minimum" bonded area are included in Table XV. It is apparent that a considerable difference exists between these areas because of the marked difference in the way in which they were determined. Whereas the "maximum" value obtained using the B.E.T. area of the exposed butanol sheets is considerably too high, the "minimum" area determined using the spray-dried pulps is believed to be only slightly low.

In order to determine if the B.E.T. area of 0.81 sq. m. per gram obtained for the spray-dried unbeaten pulp appears to be close to the actual water-dried specific surface area of the pulp, the external specific surface was estimated in several other ways. A plot was made of the B.E.T. areas and the specific scattering coefficients of unbeaten pressed pulp sheets against wet pressure and the area values resulting when these curves were extrapolated to zero pressure were determined. This has been done in Figure 24 for sulfite handsheets formed from unbeaten pulp pressed at 1, 10, 50, and 150 p.s.i. employing the values given in Table XII. The curve for the B.E.T. area was extrapolated to zero pressure and the area value read directly. For the specific scattering coefficients, the plot

when similarly extrapolated gave 384 sq. cm. per gram and the area corresponding to this value was read from Figure 23. These results appear in Table XVI.

TABLE XVI

SPECIFIC SURFACE AREA OF DRY UNBEATEN SULFITE PULP ESTIMATED IN DIFFERENT WAYS

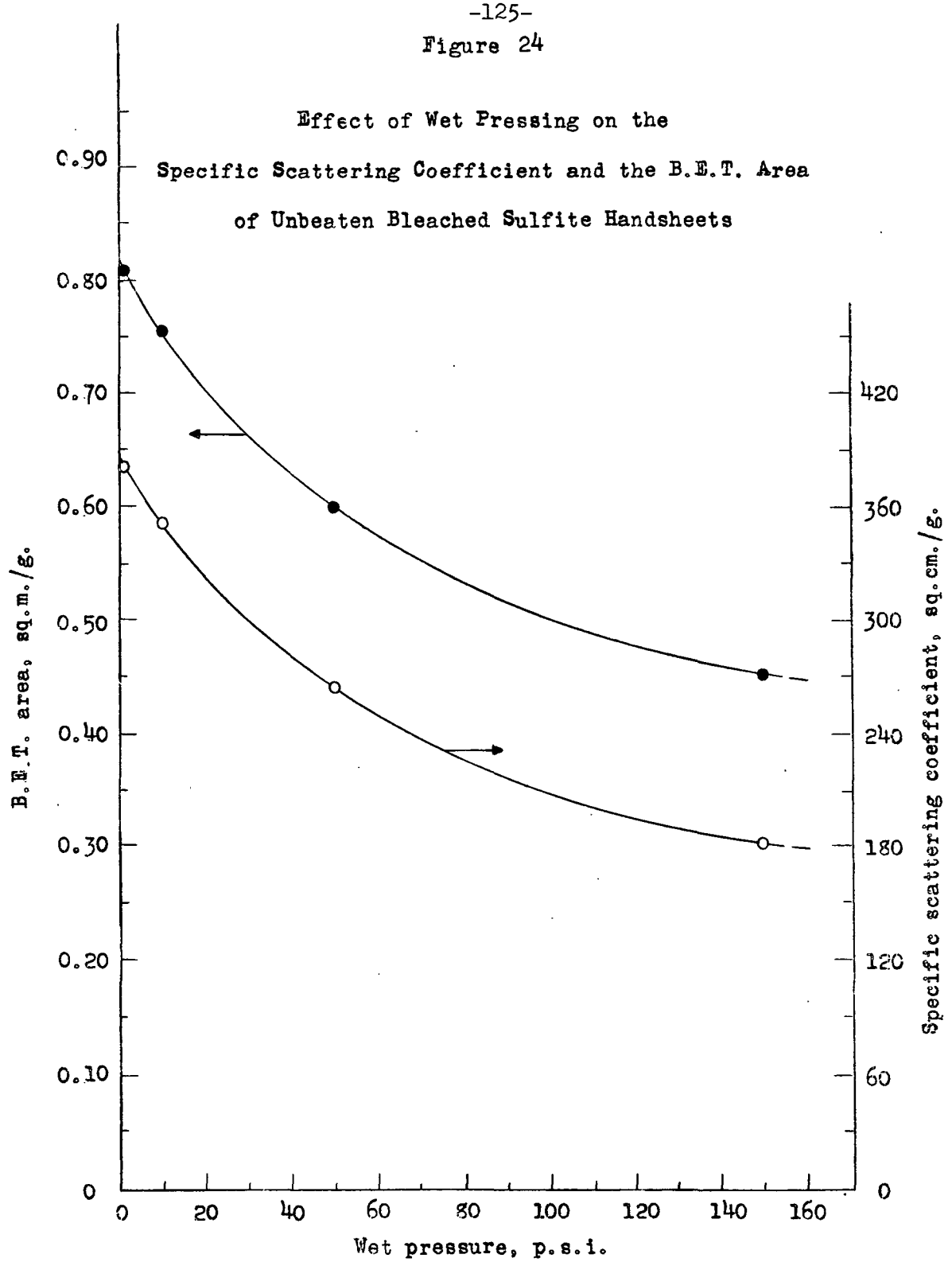
Procedure used in Obtaining Estimate	Estimated Specific Surface of Dry Fibers, sq. m./g.
B.E.T. area of spray-dried fibers	0.81
Extrapolation of B.E.T. area-wet pressure plot for unbeaten handsheets to zero pressure	0.82
Extrapolation of specific scattering coefficient-wet pressure plot to zero pressure and use of Figure 23 to obtain B.E.T. area	0.85
Extrapolation of tensile strength-B.E.T. area plot to zero tensile strength	0.84

The other method which was employed for an estimation of the dry specific surface area of the unbeaten pulp involved plotting the B.E.T. area against tensile strength for unbeaten sulfite handsheets pressed at 1, 10, 50, 150, 400, and 4000 p.s.i. appearing in Table XII. This plot is given in Figure 25. A smooth curve results and the highest area which can be obtained by extrapolation to zero tensile strength is given in Table XVI.

It is seen from Table XVI that these extrapolated estimates of unbonded fiber area check quite well and are in each case only slightly higher than the B.E.T. area of the spray-dried fiber. The extrapolation of a plot of the B.E.T. areas and the specific scattering coefficients for the pressed handsheets to zero

Figure 24

Effect of Wet Pressing on the Specific Scattering Coefficient and the B.E.T. Area of Unbeaten Bleached Sulfite Handsheets



pressure is open to the criticism that, even without wet pressing, the surface tension forces which Campbell (85) has discussed still act to draw the fibers into contact. This is certainly true but for a sheet pressed at 1 p.s.i. the apparent density was quite low indicating that the sheet had only been compacted to a small extent by these forces. The extrapolation of the tensile strength-B.E.T. area to a zero tensile value would appear to be a more fundamentally sound method of estimating the unbonded area of the unbeaten fibers comprising the hand-sheets. Although these extrapolation methods have been discussed mainly to demonstrate that the area of the spray-dried fiber is very close to what appears to be the true specific surface of the unbeaten sulfite pulp, it is very possible that one or more of these techniques may prove more useful for this porpose. At the present time, it is not of primary importance which method is the most satisfactory but rather that they all yield quite similar results. It is felt that this series of estimates constitutes valuable evidence that the specific surface area of the dry unbeaten sulfite pulp which was studied is very close to 0.81 to 0.85 sq. m. per gram.

Even if a value of 0.84 sq. m. per gram is taken as the dry specific surface of the pulp, it is still considerably lower than the 1.26 sq. m. per gram measured for the wet specific surface of the same pulp by the silvering method. Also, the value of 382 sq. cm. per gram for the specific scattering coefficient corresponding to 0.84 sq. m. per gram in Figure 23 is markedly lower than the 565 sq. cm. per gram obtained for the coefficient of the butanol sheets of the unbeaten pulp. Interestingly enough, the ratio of the dry B.E.T. area to the silvered area and the extrapolated specific scattering coefficient of the water-dried sheets to that of the butanol sheets is 0.67 and 0.68, respectively. It should be recalled also that Leech (54) found that the ratio of the specific scattering coefficient for

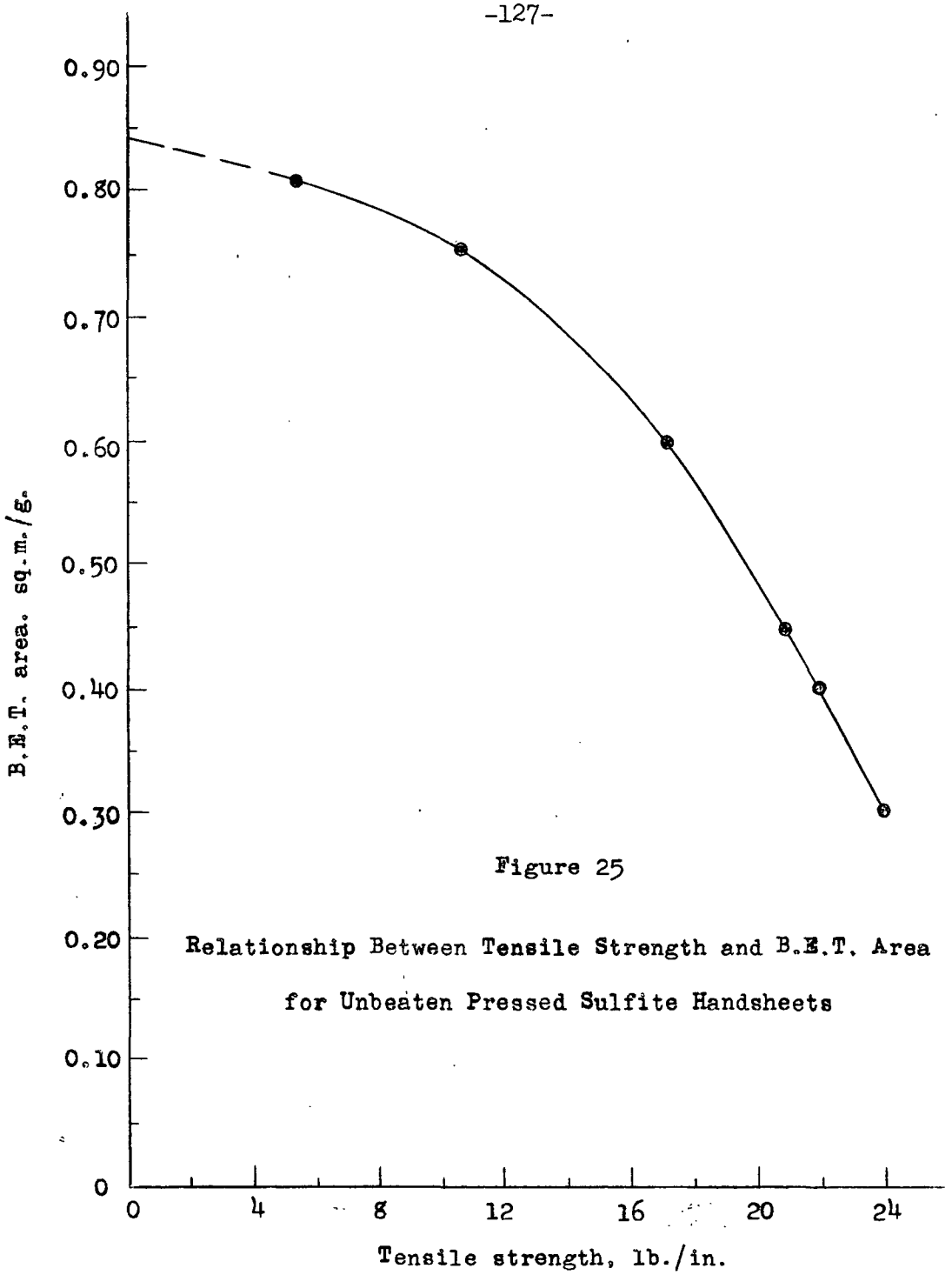


Figure 25

Relationship Between Tensile Strength and B.E.T. Area for Unbeaten Pressed Sulfite Handsheets

water-dried unbonded sulfite pulp fibers to that for benzene-dried unbonded fibers was 0.59. Although there is the possibility that this similarity of values is merely coincidence, it is not believed that such is the case. Rather, it is felt that this is an indication of the nature of the structure and surface characteristics of wet, water-dried, and butanol-dried fibers. The reasons for this belief are as follows:

It has been the contention of Clark (86) and others that in addition to large fibrils, the surface of even a slightly beaten fiber is covered with a submicroscopic fuzz made up of fine fibrils and microfibrils attached to the main fiber or the large fibrils at one end. If such is the case, then when the pulp is suspended in water the fibers are swollen, the surface of the fibers probably contains some exposed pores, and the surface fibrils are in an unbonded extented condition. Except for the very fine pores, most of this large surface is available to be silvered when the area of the pulp is determined by the surface catalytic method. When these water-wet fibers are dried, it seems reasonable to believe that surface tension and hydrogen bonding forces will act to shrink the fibers, close up the accessible pores, and largely collapse and bond the surface fibrils to the surface of the parent fiber. If, on the other hand, the water is displaced with acetone and the acetone is in turn replaced with butanol before drying, the condition of the fibers will probably be quite different. Because of the low swelling effect of butanol only a slight shrinkage of the fibers would occur, the larger surface pores would not be closed, and because of the absence of conditions promoting hydrogen bonding, the surface fibrils would probably remain in an erect unbonded position capable of pronounced light scattering. In other words, when either wet with water or dried from butanol, it is felt that the fibers are in

much the same condition since they have a high "swollen" area and unbonded, exposed surface fibrils whereas the fibers dried from water do not. If the condition of the fibers actually is as has been depicted, then the finding that the ratio of the dry fiber area to the wet fiber area is similar to the ratio of the specific scattering coefficient of the unbonded, unbeaten fibers dried from water to that of the butanol-dried fibers would logically follow.

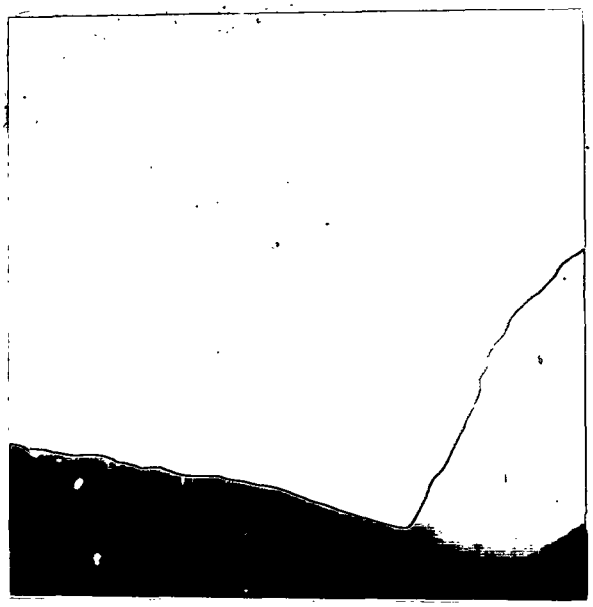
It was felt that if large protruding surface fibrils and submicroscopic fuzz are at least partially responsible for the marked differences noted in the B.E.T. areas and optical properties of water-dried and butanol-dried unbonded fibers, then a difference should be observed when the surface of the two types of fibers are studied with an optical or an electron microscope. Lightly-beaten (5 min. in a laboratory beater) sulfite pulp fibers both dried from butanol and spray dried from water were examined at high magnification with an optical microscope using both regular and dark-field illumination. No marked difference was noted. However, after a number of both types of fibers were carefully examined, it appeared as if the butanol-dried fibers had a slightly greater quantity of surface debris and that they generally seemed to be slightly less translucent than the water-dried fibers.

When, on the other hand, the fibers were observed with an electron microscope, a striking difference was noted. Work was at first done with untreated water-dried and butanol-dried fibers but because the electron beam caused the collapse of some of the extended fibrils probably because of static charging effects, the fibers were shadowed at 90 degrees with aluminum. Examples of what was seen with the electron microscope at 8000 diameters are given in Figure 26. The surface of

the slightly-beaten, butanol-dried fibers were in some places fairly smooth but very frequently extensive surface fibrillation of the type shown in Figure 26 was observed. The surface of the slightly-beaten, water-dried fibers, however, was almost entirely free of projecting fibrils and at no time during the inspection of the surface of many such fibers was any fibrillation seen which was comparable to that frequently detected on the fibers which had been dried from butanol. If the electron micrograph of the butanol-dried, aluminum-shadowed pulp fiber is carefully examined, it will be seen that the fibrillation is of two types. In addition to the large and small fibrils which protrude from the surface of the main fiber, there also appears to be (see the upper portion of the photograph) a very fine fuzz which can be observed on the surface of a fibril. This extremely fine fibrillation can also be occasionally detected when the surface of the other fibrils is inspected.

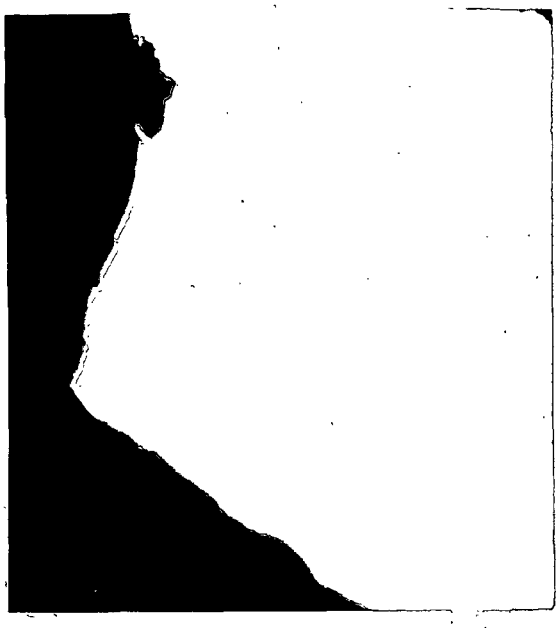
From these results, there can be little doubt that water-dried and butanol-dried unbonded fibers differ considerably in the condition of their surfaces. The many fibrils which range in size from large to extremely fine which have been observed on the surface of the butanol-dried fibers must certainly be partially responsible for the high optical scattering exhibited by these fibers. Whereas surface porosity and overall shrinkage effects are probably also influential in causing the differences noted in the water-dried and butanol-dried fibers, it was concluded that the observed divergencies in surface characteristics also contribute to a marked degree.

When the results of these studies with the electron microscope are considered, and when it is recalled that the ratio of the specific scattering coefficient of the water-dried unbonded fibers to that for the benzene-dried fibers found by Leech (54) and to butanol-dried fibers found in the present work is in the range



Dried from Water

Dried from Butanol



Dried from Water and
Aluminum Shadowed at 90 Degrees

Dried from Butanol and
Aluminum Shadowed at 90 Degrees

Figure 26

Electron Micrographs of Bleached Spruce Sulfite Pulp Beaten for Five Minutes in a Laboratory Beater

8000 Diameters

of 0.58 to 0.68, it seems grossly incorrect to take the entire difference in the specific scattering coefficients of butanol and regular handsheets as being due to differences in bonded area. Since the regular optical method does just this, there is good reason to believe that the resulting area values are higher than the true bonded area. Although it has been shown that the estimated specific scattering coefficient of an unbonded water-dried sheet of unbeaten pulp is approximately two-thirds of that for the corresponding butanol sheet, it is not known whether this ratio would continue to apply for beaten pulps. Leech's work with fractionated beaten sulfite fibers indicates that this may be the case. Therefore, a method of empirically correcting the specific scattering coefficients of the butanol sheets suggests itself on the grounds that such a step would seem to permit more accurate values of percentage bonded area to be determined. For the unbeaten pulp used in the present work the coefficient measured on the butanol-dried sheets was multiplied by approximately 0.67 and this was employed as the scattering value of the water-dried unbonded fibers. (For other pulps, there is reason to believe that the correction factor may be as great as 0.99). The use of the silver area of the pulp is no longer necessary to obtain an estimate of numerical bonded area since a linear plot of B.E.T. area against specific scattering coefficient for the water-dried sheets of the type given in Figure 23 can be used for this purpose.

Comparison of the Various Estimates of Bonded Area

Various estimates of the percentage bonded area of the regular handsheets were computed employing the B.E.T. areas and specific scattering coefficients of the water-dried and butanol-dried handsheets, the B.E.T. areas of spray-dried pulp fibers, and the silvered areas of the pulps. Included in Table XVII are estimates obtained by the regular optical method, by a modified optical method in

which the specific scattering coefficients of the butanol sheets have been multiplied by a fixed correction factor, and by the "minimum" and "maximum" techniques previously discussed.

TABLE XVII

PERCENTAGE BONDED AREA AS ESTIMATED IN VARIOUS WAYS

	Beating Time, min.			
	0	5	12	24
Regular optical method, %	51	63	75	87
Optical method employing corrected scattering coefficients of butanol sheets, %	26	45	63	81
Employing B.E.T. areas of spray-dried pulps and water-dried handsheets; "minimum", %	19	41	55	78
Employing B.E.T. areas of exposed butanol sheets and water-dried handsheets; "maximum", %	72	80	84	92

It is seen that the "maximum" values of bonded area are somewhat higher than those determined by all other methods especially for the unbeaten and slightly beaten pulp sheets. From these results, it was concluded that the values obtained from the difference in the B.E.T. area of the water-dried handsheets and the butanol handsheets exposed to 96.7% R.H. do not constitute a useful estimate of bonded area. The "minimum" values of bonded area arrived at by taking the difference in the B.E.T. areas of the water-dried handsheets and the spray-dried fibers are lower, in all instances, than the other estimates. Although the spray-dried beaten pulps are thought to be bonded to some extent, the percentage bonded

areas determined in this manner are seen to increase in a reasonable fashion as beating proceeds. Generally, it would seem that the spray drying-B.E.T. area technique provides a fairly good estimate of bonded area if it is kept in mind that it is somewhat on the low side. These estimates of "minimum" and "maximum" bonded area, then, set the limits for each set of handsheets between which the true bonded area almost certainly lies. With regard to the use of nitrogen adsorption for bonded area determinations, it should be noted that the technique itself appears to be completely applicable. The trouble arises solely from the difficulty involved in obtaining water-dried unbonded fibers, especially from beaten pulps, so that the total external surface of the pulp fibers can be determined from adsorption measurements.

The bonded areas computed by the regular optical method vary from 51% for the unbeaten pulp handsheets to 87% for the handsheets formed from pulp which had been beaten for 24 minutes. Although the percentage bonded area obtained for the unbeaten pulp sheets is somewhat higher than that found by Parsons (50) and Leech (54) for other sulfite pulps, the results are quite similar for the beaten pulp sheets. This surprisingly high value of approximately 50% of the total area of the unbeaten fibers entering into bonding was also found by Ratliff (51) in his work on kraft pulps and was one of the main reasons that Mason (84) has been critical of the optical method.

The present study has indicated that this criticism is justified and that the error in the regular optical method lies in the assumption that unbonded butanol-dried fibers have the same specific scattering coefficient as the same unbonded fibers dried from water. It has been shown that this is not the case and that a falsely high value of bonded area is apt to result when the method is used. Since

there is no way yet available to obtain sheets of water-dried pulp fibers which are known to be completely unbonded, a method has been described whereby the specific scattering coefficient of the butanol sheets can be suitably corrected. The correction factor for the unbeaten sulfite pulp was shown to be approximately 0.67 and it was assumed that this factor would not be altered appreciably when the pulp was beaten. The corrected optical values of bonded area are given in Table XVII. Generally these areas are seen to be considerably lower than the values determined with the regular optical method. It should also be noted that although the corrected optical area is greater in each case than the "minimum" areas, the two estimates appear to parallel each other quite well.

Additional study is required, of course, to check the proper correction factor to employ for the beaten pulps used in the present work and any other pulps to which the method is applied. To summarize briefly, this can be done by forming a number of handsheets from the pulp in question and subjecting them to a series of wet pressures starting at a lower limit of about 1 p.s.i. Regular butanol sheets are also prepared from the same pulp and the specific scattering coefficients of all the handsheets are determined. A plot of specific scattering coefficient against wet pressure as is done in Figure 24 permits the extrapolated value of the coefficient to be obtained at zero pressure. Another and possibly more accurate way of handling this extrapolation is to measure the tensile strength of the pressed sheets and plot the specific scattering coefficient against tensile strength. Extrapolation of this plot to zero tensile strength gives the desired value of the coefficient. Regardless of which of these methods is employed to obtain an estimate of the specific scattering coefficient of the unbonded water-dried fibers, the desired correction factor is obtained by dividing the extrapolated

coefficient by the specific scattering coefficient of the butanol sheets.

Pending further investigation, it is felt that the use of suitably corrected values of the specific scattering coefficient for the butanol sheets provides an easy method of obtaining an estimate of the bonded area of standard handsheets which is considerably closer to the true bonded area of these sheets than can be determined by the optical method as it has been commonly employed.

SUMMARY AND CONCLUSIONS

The present investigation has dealt with: (1) the nature of the adsorption of nitrogen, n-butane, and carbon dioxide on sprucewood and its components, and (2) the application of gas adsorption techniques to the study of the internal and external area of pulp and the bonded area of paper.

Volume-pressure studies made with n-butane indicated that values which have been commonly employed at 0 and 23°C. for correction of this gas for deviation from the perfect gas laws are somewhat high. New values have been determined and used.

In all cases, S-shaped isotherms were obtained for the adsorption of nitrogen and n-butane on water-dried specimens of extracted sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose near or below the liquefaction temperature of the adsorbate. Little or no hysteresis was observed. The adsorption curves were duplicated after evacuation, indicating that no reaction took place between the gas and the adsorbent, and also that the original external area of the adsorbent was not altered by the adsorption-desorption cycle.

Whereas the B.E.T. and the Harkins-Jura methods proved to be wholly satisfactory for the estimation of surface area from the adsorption data, the Fu-Bartell method could not be applied in all cases. When area estimates were obtained, they were usually considerably lower than the areas determined by the other methods. It was felt that these results are not due to any fundamental error in the Fu-Bartell method but rather to the fact that a method which is based on the assumption that the adsorbent is highly porous apparently cannot be successfully applied to nonporous materials.

For nitrogen adsorption, the check between the areas determined by the B.E.T. and the Harkins-Jura methods was best when the cross-sectional area of a nitrogen molecule was taken as 15.7 sq. A. The molecular area for n-butane which gave the best check with the B.E.T. nitrogen areas (molecular area--16.2 sq. A.) was 35.4 sq. A.

Decrease in free surface energy and differential heat of adsorption curves for n-butane and nitrogen indicate that the behavior of the adsorbed gas film was not appreciably affected when the sprucewood was delignified or when the chlorite holocellulose was extracted with alkali and that, in all instances, only physical adsorption was occurring.

Equilibrium studies of the uptake of carbon dioxide at -78.6°C. by sprucewood, chlorite holocellulose, KOH-extracted chlorite holocellulose, precipitated hemicelluloses, and spruce native lignin showed that adsorption equilibrium was quickly reached only for the KOH-extracted holocellulose. From area determinations after exposure to the carbon dioxide and from an investigation of the energy of activation associated with the initial sorption, it was concluded that the observed prolonged uptake of carbon dioxide was most probably due to a solution of the gas by the noncellulosic components of the wood.

Isotherms were determined for the adsorption and desorption of carbon dioxide on KOH-extracted holocellulose at -78.6°C. A marked hysteresis loop was obtained although from the points on the lower part of the desorption curve it appears that the carbon dioxide was completely removed on evacuation. When a second run was made on the same sample, both the adsorption and desorption curves were duplicated.

Comparison of the carbon dioxide monolayer volume with that for nitrogen

(molecular cross-sectional area--16.2 sq. A.) on the KOH-extracted chlorite holocellulose gave a value of 28.3 sq. A. for the area occupied by an adsorbed carbon dioxide molecule.

The change in free surface energy for the adsorption of carbon dioxide on the KOH-extracted chlorite holocellulose was much the same as for nitrogen and n-butane on the same adsorbent. The differential heat of adsorption was quite high for the first adsorption of gas but fell to an apparently steady value at the higher relative pressures which is considerably lower than the normal heat of sublimation of solid carbon dioxide at -78.6°C. The proposal was made that this low differential heat value may be an indication that the carbon dioxide molecules adsorbed in the second and higher layers exist in a state corresponding more closely to a liquid than to a solid. On the other hand, the large hysteresis loop noted during the adsorption-desorption studies, the fairly high values for the apparent molecular area, and the high differential heats at low adsorbed volumes all indicate that a relatively strong attraction exists between the first layer of adsorbed carbon dioxide molecules and the cellulose. It was proposed that this increased attraction resulted from hydrogen bonds forming between the oxygens of the carbon dioxide molecules and the free cellulosic hydroxyl groups.

The results of the adsorption studies with nitrogen, n-butane, and carbon dioxide demonstrated that either nitrogen or n-butane are satisfactory for area studies on cellulosic materials. Of the two gases, however, nitrogen gives adsorption measurements having somewhat better precision, its molecular area is more definitely known, and it essentially behaves as a perfect gas at room temperature. Although both the B.E.T. and the Harkins-Jura methods of area estimation have been found to give satisfactory results in the present work, the B.E.T. method

gave better straight-line plots and required the measurement of fewer points on the adsorption isotherm. Therefore, it was concluded that nitrogen adsorption measurements and the B.E.T. method of computing surface area constitute the best combination for area studies on pulp and paper using gas adsorption techniques.

When adsorption and desorption isotherms were determined with nitrogen at -195.6°C. on benzene-dried specimens of sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose, an S-shaped curve was obtained only for the sprucewood. The isotherms for the other materials were so-called type IV which are commonly found for highly porous adsorbents. The areas of the sprucewood, chlorite holocellulose, and KOH-extracted chlorite holocellulose, as computed by the B.E.T. method, were 4.0, 61.3, and 62.2 sq. m. per gram, respectively.

Pore volume distributions were determined for the chlorite and KOH-extracted holocellulose from these adsorption data by the Wheeler-Shull method. The distribution curves obtained indicated that the greater part of the adsorption of nitrogen took place in pores 10 to 100 A. in diameter. Extraction of the chlorite holocellulose with alkali and the subsequent removal of a large portion of the hemicelluloses acted to increase slightly the total pore volume and the average pore size. The pore size information obtained in this study constitutes additional evidence of the size range of the narrow pores and channels between the microfibrils and crystallites of cellulose. The similarity between the shape and maxima in the volume distribution curves for the chlorite and KOH-extracted holocellulose and similar curves for cotton linters reported in the literature indicates that the submicroscopic structure of cotton and purified wood cellulose is much the same.

When specimens of benzene-dried, KOH-extracted chlorite holocellulose similar to that used for the pore volume investigation were permitted to absorb increasing

amounts of moisture and were redried, it was found that the high initial internal area as determined by nitrogen adsorption was markedly decreased by moisture takeup and that the original water-dried area was approached but not reached as the material was exposed to relative humidities near 100%.

A number of regular handsheets were prepared from bleached spruce sulfite pulp in which the bonded area had been varied by different degrees of wet pressing and by beating the pulp from which they were formed. Nitrogen adsorption-B.E.T. areas and specific scattering coefficients were determined on these sheets and it was found that an excellent linear correlation existed between the two determinations. From these results, it was concluded that the relative unbonded area of water-dried handsheets can be quickly and easily obtained from measurements of the specific scattering coefficient.

Unbonded water-formed handsheets were prepared from unbeaten pulps by displacing the water with acetone and the acetone with butanol and with benzene. The specific scattering coefficient of the benzene sheets was approximately 10% greater than that of the butanol sheets both before and after absorption of over 24% moisture and redrying. The takeup of moisture by the sheets markedly decreased the B.E.T. area but only slightly reduced the scattering properties. It was concluded that the higher specific scattering coefficient of the benzene sheets was not due to less fiber-to-fiber bonding and that butanol sheets were the more satisfactory for use with the optical method of estimating bonded area.

Several promising methods of preparing essentially unbonded, water-dried fibers were investigated, and a method involving the spraying and drying of fibers on a sheet of polythene was selected as being the most satisfactory.

An investigation was undertaken of the question of bonded area and its measurement. Several different methods of estimating bonded area were proposed, critically considered, and employed for the estimation of the bonded area of unbeaten and beaten bleached sulfite handsheets. The work on specific surface area, optical properties, and B.E.T. areas of the various pulps and handsheets necessary for these area estimates led to the following main conclusions:

1. The bonded area estimated from the difference in the B.E.T. areas of the water-dried handsheets and the butanol sheets which have been dried after exposure to 96.7% R.H. represents a "maximum" value.

2. The estimate of bonded area obtained from the difference in the B.E.T. areas of the water-dried handsheets and the specimens of spray-dried pulp fibers can be taken as a "minimum" value.

3. The B.E.T. area of the spray-dried unbeaten pulp was checked very well by the values obtained on extrapolation of a plot of the B.E.T. area of the pressed unbeaten handsheets against wet pressure to zero pressure and a B.E.T. area-tensile strength plot to zero tensile.

4. The specific surface area of the dry unbeaten pulp fibers was considerably lower than the silvered area of the same pulp.

5. The estimated specific scattering coefficient of the unbonded, water-dried, unbeaten fibers was considerably lower than that for the same fibers dried from butanol but may bear a fairly constant relationship to it.

6. Because of the markedly higher scattering properties of the unbonded butanol-dried fibers than the unbonded water-dried fibers, the bonded area measured by the regular optical method would appear to be erroneously high.

Unbonded fibers of slightly-beaten sulfite pulp which had been dried from butanol and from water were observed with an electron microscope. This work demonstrated that the surface characteristics of these materials were quite different in that the water-dried fibers showed negligible surface fibrillation whereas the fibers dried from butanol showed numerous groups of protruding surface fibrils in addition to evidences of an erect submicroscopic fuzz.

Percentage bonded areas of the unbeaten and beaten pulp handsheets were estimated by the optical method and by means which gave "minimum" and "maximum" values. A method was suggested and used whereby the specific scattering coefficients of the butanol sheets were multiplied by a constant fractional correction factor. When these corrected values were employed, estimates of bonded area were obtained which paralleled quite closely the spray drying-B.E.T. area "minimum" bonded areas. After careful consideration of the results of the bonded area studies, it was concluded that this corrected optical method gave percentage bonded areas which were considerably closer to the true values for the handsheets than were obtained by the optical method as it is usually employed.

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APPENDIX

TABLE A

ADSORPTION OF NITROGEN AND n-BUTANE ON SPRUCEWOOD

Nitrogen adsorption

at -195.7°C.			at -182.9°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
3.9	0.0051	0.097	7.3	0.0026	0.053
17.7	0.023	0.173	29.0	0.011	0.107
42.4	0.055	0.223	58.8	0.0212	0.141
78.4	0.102	0.257	93.9	0.034	0.166
115.8	0.151	0.288	132.5	0.048	0.186
154.8	0.202	0.314	176.3	0.064	0.205
193.0	0.251	0.336	223.3	0.081	0.219
231.3	0.301	0.361	267.5	0.097	0.233
272.1	0.354	0.383	308.0	0.112	0.244
313.5	0.408	0.406	352.4	0.128	0.256
356.3	0.464	0.438	397.8	0.145	0.266
399.8	0.521	0.466	439.7	0.160	0.276
443.8	0.578	0.499	483.9	0.176	0.286
487.0	0.634	0.539	529.0	0.192	0.298
534.8	0.697	0.590	572.7	0.208	0.306
576.0	0.751	0.643	616.0	0.224	0.310
612.4	0.797	0.693	657.2	0.238	0.317
641.6	0.835	0.766	701.5	0.255	0.328
662.4	0.863	0.870	730.7	0.265	0.333
695.5	0.906	1.04			
707.9	0.922	1.16			
Desorption					
696.0	0.906	1.06			
664.9	0.865	0.892			
602.9	0.784	0.707			
503.2	0.655	0.565			
342.6	0.446	0.438			
230.9	0.301	0.369			

TABLE A (Continued)

ADSORPTION OF NITROGEN AND n-BUTANE ON SPRUCEWOOD

n-Butane adsorption

at 0°C.			at -21.2°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
24.4	0.029	0.016	8.9	0.027	0.016
47.5	0.061	0.030	25.6	0.078	0.040
75.5	0.097	0.043	53.2	0.164	0.071
101.6	0.131	0.056	84.3	0.260	0.100
130.9	0.169	0.070	122.5	0.376	0.131
163.0	0.210	0.085	162.7	0.501	0.161
207.4	0.268	0.101	202.2	0.622	0.197
265.5	0.343	0.117	243.6	0.747	0.257
339.7	0.438	0.136	274.5	0.844	0.346
423.0	0.546	0.165	294.0	0.905	0.482
495.6	0.640	0.202			
566.8	0.731	0.241			
622.8	0.804	0.289			
663.8	0.857	0.349			
700.0	0.903	0.449			
730.0	0.942	0.639			
Desorption					
722.9	0.933	0.598			
689.3	0.889	0.436			
634.0	0.818	0.319			
562.0	0.725	0.247			
482.3	0.622	0.201			
402.1	0.519	0.168			
319.5	0.412	0.139			
241.1	0.311	0.113			
172.2	0.222	0.089			

TABLE B

ADSORPTION OF NITROGEN AND n-BUTANE ON CHLORITE HOLOCELLULOSE

Nitrogen adsorption

at -195.7°C.			at -182.9°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
2.6	0.0033	0.083	5.9	0.0022	0.044
11.1	0.014	0.136	20.8	0.0076	0.082
38.4	0.049	0.192	43.8	0.016	0.111
75.8	0.097	0.231	72.7	0.027	0.134
117.1	0.150	0.259	106.1	0.039	0.155
158.3	0.203	0.282	144.0	0.052	0.170
202.5	0.260	0.306	184.8	0.067	0.184
249.2	0.319	0.326	227.4	0.083	0.197
298.5	0.382	0.349	272.6	0.100	0.207
352.8	0.451	0.377	317.1	0.116	0.218
403.8	0.516	0.403	362.6	0.132	0.228
457.7	0.585	0.438	407.6	0.149	0.234
510.9	0.652	0.479	453.8	0.165	0.244
572.6	0.732	0.541	499.3	0.182	0.252
628.7	0.804	0.626	543.7	0.198	0.259
671.4	0.857	0.721	588.4	0.214	0.264
699.9	0.900	0.855	632.5	0.231	0.274
720.1	0.922	0.978	674.1	0.246	0.281
			715.8	0.261	0.285
Desorption			744.0	0.272	0.292
700.6	0.898	0.858			
660.1	0.846	0.705			
571.3	0.732	0.541			
432.0	0.553	0.419			
289.5	0.370	0.338			
127.7	0.164	0.262			

TABLE B (Continued)

ADSORPTION OF NITROGEN AND n-BUTANE ON CHLORITE HOLOCELLULOSE

n-Butane adsorption

at 0°C.			at -21.2°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
31.8	0.041	0.017	12.5	0.039	0.018
62.9	0.081	0.031	30.0	0.092	0.038
91.4	0.118	0.043	55.0	0.169	0.061
124.1	0.160	0.055	82.1	0.253	0.083
163.4	0.211	0.068	113.7	0.350	0.106
210.2	0.271	0.082	146.7	0.451	0.128
256.7	0.331	0.095	179.1	0.551	0.153
319.2	0.411	0.112	216.5	0.666	0.190
377.9	0.487	0.129	247.3	0.761	0.235
434.9	0.560	0.147	273.1	0.840	0.301
496.0	0.639	0.170	291.1	0.896	0.390
557.8	0.719	0.199	301.9	0.929	0.487
618.1	0.797	0.242			
675.9	0.871	0.316			
707.4	0.912	0.400			
723.7	0.933	0.477			
Desorption					
700.0	0.901	0.382			
617.6	0.796	0.249			
422.3	0.544	0.145			
245.9	0.317	0.089			
142.4	0.184	0.056			
83.0	0.107	0.034			

TABLE C

ADSORPTION OF NITROGEN AND n-BUTANE ON KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Nitrogen adsorption

at -195.7°C.			at -182.9°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
7.0	0.0090	0.120	20.7	0.0075	0.081
27.6	0.036	0.185	44.3	0.016	0.114
57.3	0.074	0.224	75.9	0.028	0.143
91.2	0.118	0.251	112.5	0.041	0.163
129.2	0.166	0.276	152.5	0.055	0.181
174.8	0.225	0.297	194.1	0.071	0.198
224.2	0.289	0.324	238.2	0.087	0.209
274.6	0.354	0.352	282.8	0.103	0.220
328.2	0.419	0.377	329.1	0.119	0.229
384.1	0.490	0.407	377.1	0.137	0.241
443.1	0.564	0.444	428.5	0.156	0.250
500.8	0.638	0.488	479.9	0.174	0.261
557.0	0.710	0.546	533.3	0.194	0.267
616.3	0.784	0.642	584.8	0.212	0.279
669.8	0.852	0.769	635.6	0.231	0.291
701.0	0.891	0.911	690.0	0.251	0.299
722.2	0.916	1.07	724.4	0.264	0.305
			748.3	0.272	0.308
Desorption					
699.6	0.888	0.929			
652.5	0.828	0.735			
561.3	0.712	0.565			
395.2	0.502	0.418			
261.2	0.331	0.339			
172.3	0.218	0.296			

TABLE C (Continued)

ADSORPTION OF NITROGEN AND n-BUTANE ON KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Butane adsorption

at 0°C.			at -21.2°C.		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
35.6	0.046	0.020	23.7	0.074	0.031
62.0	0.080	0.031	49.6	0.153	0.061
96.1	0.124	0.048	83.1	0.226	0.090
137.4	0.177	0.065	123.2	0.379	0.119
181.4	0.234	0.083	169.2	0.521	0.151
225.4	0.291	0.097	209.9	0.646	0.189
270.0	0.348	0.110	241.8	0.753	0.233
323.5	0.417	0.126	275.1	0.846	0.316
378.9	0.489	0.142	292.1	0.899	0.407
434.1	0.560	0.161	301.5	0.928	0.508
492.8	0.636	0.184			
555.8	0.717	0.218			
623.3	0.804	0.270			
674.9	0.871	0.345			
707.2	0.913	0.445			
726.1	0.937	0.535			
736.5	0.950	0.615			
Desorption					
698.1	0.901	0.450			
646.5	0.843	0.316			
412.1	0.532	0.155			
242.5	0.313	0.099			
141.9	0.183	0.066			

TABLE D

B.E.T. DATA FOR NITROGEN ADSORPTION AT -195.7°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
p/p_o	$p/v_g(p_o-p)$, g./ml.	p/p_o	$p/v_g(p_o-p)$, g./ml.	p/p_o	$p/v_g(p_o-p)$, g./ml.
0.055	0.260	0.049	0.267	0.074	0.364
0.102	0.440	0.097	0.467	0.118	0.529
0.151	0.619	0.150	0.681	0.168	0.721
0.202	0.806	0.203	0.901	0.225	0.975
0.251	0.999	0.260	1.15	0.289	1.25
0.301	1.19	0.319	1.44		

TABLE E

HARKINS-JURA DATA FOR NITROGEN ADSORPTION AT -195.7°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
p/p_o	$1/v_g^2$, $(g./ml.)^2$	p/p_o	$1/v_g^2$, $(g./ml.)^2$	p/p_o	$1/v_g^2$, $(g./ml.)^2$
0.251	8.85	0.260	10.7	0.289	9.52
0.301	7.69	0.319	9.43	0.354	8.06
0.354	6.80	0.382	8.20	0.419	7.04
0.408	6.06	0.451	7.04	0.490	6.02
0.464	5.21	0.516	6.17	0.564	5.08
0.521	4.61	0.585	5.21	0.638	4.20
0.578	4.02	0.652	4.37	0.710	3.36
0.634	3.44	0.732	3.41	0.784	2.43
0.697	2.87	0.804	2.55	0.852	1.69
0.751	2.42	0.857	1.92	0.891	1.20
0.797	2.07	0.922	1.05		
0.835	1.69				
0.887	1.12				
0.922	0.75				

TABLE F

FU AND BARTELL DATA FOR NITROGEN ADSORPTION AT -195.7°C.

p/p_o	$a\Phi$, ergs/g.($\times 10^{-5}$) Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
0.05	1.49	1.38	1.44
0.10	1.96	1.80	1.89
0.15	2.26	2.08	2.18
0.20	2.50	2.30	2.40
0.25	2.71	2.48	2.56
0.30	2.90	2.66	2.72
0.35	3.04	2.81	2.87
0.40	3.22	2.96	3.01
0.45	3.36	3.08	3.14
0.50	3.52	3.20	3.26
0.55	3.64	3.31	3.37
0.60	3.75	3.42	3.48
0.65	3.88	3.52	3.60
0.70	3.99	3.63	3.71
0.75	4.10	3.74	3.82
0.80	4.22	3.85	3.93
0.85	4.35	3.96	4.06
0.90	4.48	4.09	4.19

TABLE G

B.E.T. DATA FOR n-BUTANE ADSORPTION AT 0°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
p/p_o	$p/v_g(p_o-p)$, g./ml.	p/p_o	$p/v_g(p_o-p)$, g./ml.	p/p_o	$p/v_g(p_o-p)$, g./ml.
0.061	2.15	0.062	2.72	0.080	2.43
0.117	2.61	0.081	2.87	0.124	2.79
0.149	2.70	0.118	3.13	0.140	3.08
0.169	2.90	0.160	3.44	0.177	3.33
0.210	3.15	0.211	3.94	0.234	3.68
0.268	3.62	0.271	4.51	0.291	4.23
0.302	3.95				

TABLE H

HARKINS-JURA DATA FOR n-BUTANE ADSORPTION AT 0°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
p/p_o	$1/v_g^2$, $(g./ml.)^2$	p/p_o	$1/v_g^2$, $(g./ml.)^2$	p/p_o	$1/v_g^2$, $(g./ml.)^2$
0.343	73.0	0.331	110	0.291	107
0.438	54.1	0.411	80.0	0.348	82.6
0.546	36.8	0.487	60.2	0.417	62.9
0.640	24.5	0.560	46.3	0.489	49.5
0.731	17.2	0.639	34.6	0.560	38.6
0.804	12.0	0.719	25.3	0.636	29.5
0.857	8.2	0.797	17.1	0.717	21.1
0.903	5.0	0.871	10.0	0.804	13.7
		0.911	6.3	0.871	8.4
				0.937	3.5

TABLE I

FU AND BARTELL DATA FOR n-BUTANE ADSORPTION AT 0°C.

p/p_o	$a\varphi$, ergs/g. (x 10^{-5}) Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
0.05	0.27	0.23	0.22
0.10	0.51	0.42	0.42
0.15	0.73	0.61	0.60
0.20	0.94	0.78	0.79
0.25	1.14	0.94	0.96
0.30	1.33	1.09	1.13
0.35	1.51	1.23	1.30
0.40	1.68	1.37	1.45
0.45	1.83	1.51	1.61
0.50	1.98	1.66	1.76
0.55	2.13	1.79	1.90
0.60	2.29	1.92	2.05
0.65	2.44	2.07	2.20
0.70	2.60	2.21	2.35
0.75	2.77	2.35	2.51
0.80	2.95	2.49	2.67
0.85	3.14	2.65	2.85
0.90	3.36	2.85	3.06

TABLE J

LOW-PRESSURE ADSORPTION OF NITROGEN AND n-BUTANE

Sprucewood			Chlorite Holocellulose			KOH-extracted Chlorite Hollocellulose		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml. (S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml. (S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml. (S.T.P.)/g.
Nitrogen at -195.7°C.								
0.8	0.0010	0.051	0.8	0.0010	0.051	1.2	0.0015	0.050
3.9	0.0051	0.097	2.6	0.0033	0.083	7.0	0.0090	0.120
17.7	0.023	0.173	11.1	0.014	0.136	27.6	0.035	0.185
			38.4	0.049	0.192			
n-Butane at 0°C.								
1.3	0.0017	0.0012	1.0	0.0013	0.0007	1.2	0.0017	0.0002
3.1	0.0040	0.0025	2.5	0.0032	0.0017	3.4	0.0044	0.0021
6.3	0.0080	0.0044	4.6	0.0059	0.0029	12.4	0.016	0.0068
13.7	0.018	0.0099	14.3	0.018	0.0082	35.6	0.046	0.0198
24.4	0.029	0.0160	31.8	0.041	0.0172			

TABLE K

CHANGE IN FREE SURFACE ENERGY

Nitrogen adsorption at -195.7°C.

p/p_o	- ΔF, ergs/sq. cm. Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
0.05	13.1	13.2	13.5
0.10	17.2	17.2	17.7
0.15	19.8	20.0	20.4
0.20	22.0	22.1	22.4
0.25	23.8	23.8	23.9
0.30	25.4	25.6	25.4
0.35	26.6	27.0	26.8
0.40	28.2	28.4	28.1
0.45	29.5	29.6	29.3
0.50	30.8	30.8	30.5
0.55	31.9	31.8	31.5
0.60	32.9	32.9	32.5
0.65	34.0	33.8	33.6
0.70	35.0	34.9	34.7
0.75	35.9	36.0	35.7
0.80	37.0	37.0	36.7
0.85	38.2	38.1	37.9
0.90	39.3	39.3	39.2

TABLE K (Continued)

CHANGE IN FREE SURFACE ENERGY

n-Butane adsorption at 0°C.

p/p_o	Sprucewood	Chlorite Holocellulose	KOH-extracted Chlorite Holocellulose
		$-\Delta F$, ergs/sq. cm.	
0.05	2.4	2.2	2.0
0.10	4.5	4.0	3.9
0.15	6.4	5.8	5.6
0.20	8.2	7.4	7.5
0.25	10.0	9.0	9.1
0.30	11.7	10.5	10.7
0.35	13.2	11.9	12.2
0.40	14.7	13.2	13.6
0.45	16.1	14.3	15.1
0.50	17.4	16.0	16.5
0.55	18.7	17.2	18.0
0.60	20.1	18.5	19.4
0.65	21.4	19.9	20.8
0.70	22.8	21.2	22.2
0.75	24.3	22.6	23.7
0.80	25.9	23.9	25.2
0.85	27.5	25.5	26.8
0.90	29.5	27.4	28.8

TABLE L

DIFFERENTIAL HEAT OF ADSORPTION

Nitrogen adsorption at -195.7 and -182.9°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
v/v_m at -195.7°C.	$-\Delta H$, kg.-cal./mole	v/v_m at -195.7°C.	$-\Delta H$, kg.-cal./mole	v/v_m at -195.7°C.	$-\Delta H$, kg.-cal./mole
0.19	2.22	0.21	2.45	0.22	2.45
0.29	2.08	0.32	2.32	0.33	2.35
0.38	1.93	0.42	2.19	0.43	2.29
0.48	1.90	0.53	2.18	0.54	2.25
0.57	1.88	0.63	2.06	0.65	2.03
0.67	1.88	0.74	1.97	0.76	1.87
0.76	1.87	0.84	1.82	0.87	1.80
0.86	1.83	0.95	1.76	0.97	1.75
0.95	1.69	1.05	1.69	1.08	1.67
1.05	1.60	1.16	1.56	1.19	1.59
1.15	1.50	1.26	1.46	1.26	1.53
1.20	1.54	1.32	1.42		
1.28	1.47				

TABLE L (Continued)

DIFFERENTIAL HEAT OF ADSORPTION

n-Butane at 0 and -21.2°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
v/v_m at 0°C.	$-\Delta H$, kg.-cal./mole	v/v_m at 0°C.	$-\Delta H$, kg.-cal./mole	v/v_m at 0°C.	$-\Delta H$, kg.-cal./mole
0.08	6.62	0.09	6.39	0.09	6.56
0.13	6.50	0.19	6.28	0.18	6.39
0.21	6.28	0.29	6.27	0.26	6.28
0.36	6.24	0.38	6.17	0.35	6.24
0.42	6.20	0.48	6.07	0.44	6.13
0.55	5.96	0.58	6.11	0.53	6.09
0.63	5.86	0.68	6.15	0.61	6.00
0.71	5.80	0.77	6.13	0.70	5.85
0.84	5.76	0.86	6.13	0.79	5.85
0.97	5.89	0.96	6.15	0.88	5.81
1.05	6.07	1.06	6.13	0.96	5.81
1.18	6.19	1.15	6.02	1.06	5.82
1.26	6.12	1.25	5.95	1.15	5.72
1.35	6.01	1.44	5.92	1.23	5.65
1.47	5.82	1.54	5.91	1.32	5.64
1.68	5.62	1.73	5.85	1.41	5.62
2.10	5.51	1.92	5.84	1.76	5.63
				2.01	5.58

TABLE M

EQUILIBRIUM DATA FOR CARBON DIOXIDE AT -78.6°C.

Sprucewood		Chlorite Holocellulose	
Duration of Exposure, min.	Manometer Reading, cm. of mercury	Duration of Exposure, min.	Manometer Reading, cm. of mercury
17	19.6	17	25.3
37	18.9	37	25.1
63	18.3	68	25.0
240	15.7	115	24.9
360	14.7	270	24.5
645	12.8	625	24.0
1265	10.6	1290	23.4
1680	9.5	2090	22.8
2730	7.6	3480	22.5
3340	6.7	4230	22.0
4200	5.9	4800	21.7
Second Run			
18	19.2	20	25.5
38	18.6	40	25.3
76	18.0	70	25.2
130	17.1	120	25.0
300	15.5	240	24.9
450	14.3	762	24.0
1440	10.9	1250	23.5

TABLE M (Continued)

EQUILIBRIUM DATA FOR CARBON DIOXIDE AT -78.6°C.

KOH-extracted Chlorite Holocellulose

Duration of Exposure, min.	Manometer Reading, cm. of mercury
17	23.5
38	23.4
63	23.4
112	23.5
180	23.4
388	23.4
720	23.3
1450	23.6
2040	23.4

Precipitated Hemicelluloses

Duration of Exposure, min.	Manometer Reading, cm. of mercury
18	15.8
40	15.2
80	15.1
200	14.6
450	13.9
1125	12.8
1800	12.1
3300	11.4

Spruce Native Lignin

Duration of Exposure, min.	Manometer Reading, cm. of mercury
18	20.8
38	19.6
78	19.3
200	19.0
480	18.7
1440	18.1
3000	17.6

TABLE N

SORPTION OF CARBON DIOXIDE ON SPRUCEWOOD

at -78.6°C.		at 0°C.	
Duration of Exposure, min.	Volume Sorbed, ml.(S.T.P.)/g.	Duration of Exposure, min.	Volume Sorbed, ml.(S.T.P.)/g.
17	0.42	18	0.82
37	0.49	36	0.97
63	0.58	65	1.12
240	0.84	108	1.24
360	0.94	187	1.36
645	1.14	360	1.50
1266	1.37	1025	1.63
1680	1.49	1700	1.67
2730	1.68	2530	1.69
4200	1.86	4560	1.71
5856	1.99	5300	1.72

TABLE O

ADSORPTION OF CARBON DIOXIDE ON
KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Adsorption at -78.6°C.

First Run			Second Run		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
1.2	0.0016	0.0035	11.0	0.015	0.016
3.2	0.0042	0.0084	46.1	0.062	0.052
13.3	0.018	0.024	108.4	0.146	0.088
34.3	0.045	0.045	182.6	0.246	0.128
71.1	0.094	0.070	266.8	0.360	0.164
118.4	0.156	0.102	354.1	0.477	0.200
171.2	0.226	0.127	440.9	0.596	0.235
227.4	0.300	0.150	525.4	0.710	0.270
285.2	0.377	0.171	607.6	0.822	0.310
349.3	0.462	0.196			
415.1	0.550	0.224			
486.3	0.645	0.246			
554.4	0.738	0.282			
617.4	0.820	0.314			
687.0	0.912	0.338			

TABLE O (Continued)

ADSORPTION OF CARBON DIOXIDE ON
KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Desorption at -78.6°C.

First Run			Second Run		
Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed ml.(S.T.P.)/g.	Equilibrium Pressure, mm. of mercury	p/p_o	Volume Adsorbed ml.(S.T.P.)/g.
674.9	0.896	0.336	575.0	0.776	0.304
609.9	0.810	0.315	491.1	0.662	0.282
521.2	0.692	0.289	386.5	0.520	0.254
425.7	0.565	0.260	273.0	0.367	0.217
323.7	0.430	0.229	160.6	0.223	0.172
220.8	0.294	0.194	72.2	0.100	0.125
110.4	0.147	0.141	33.4	0.046	0.094
49.5	0.066	0.103	16.3	0.023	0.068
			8.1	0.011	0.054
Adsorption at -89.3°C.					
7.0	--	0.036			
28.4	--	0.070			
53.7	--	0.105			
85.7	--	0.132			
117.3	--	0.162			
152.9	--	0.185			
185.0	--	0.201			
216.1	--	0.217			
246.3	--	0.236			
275.2	--	0.259			

TABLE Q

NITROGEN ADSORPTION ON BENZENE-DRIED SPECIMENS AT -195.6°C.

Sprucewood		Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.	p/p_o	Volume Adsorbed, ml.(S.T.P.)/g.
0.014	0.56	0.001	4.64	0.007	8.06
0.037	0.71	0.027	10.2	0.028	11.0
0.075	0.84	0.083	13.0	0.078	13.6
0.126	0.96	0.140	14.9	0.135	15.5
0.192	1.07	0.204	16.7	0.199	17.3
0.260	0.20	0.273	18.6	0.270	19.2
0.328	1.31	0.340	20.6	0.339	21.2
0.395	1.41	0.410	22.9	0.409	23.5
0.466	1.54	0.484	25.7	0.482	26.3
0.504	1.73	0.551	28.5	0.551	29.2
0.608	1.93	0.616	31.3	0.615	32.4
0.679	2.12	0.683	34.1	0.678	35.9
0.750	2.36	0.751	36.8	0.739	39.7
0.817	2.64	0.815	39.4	0.801	43.8
0.882	3.11	0.871	41.6	0.863	47.5
0.944	3.93	0.919	43.6	0.924	49.8
0.966	4.56	0.961	45.3	0.950	50.6
		v_s	46.9	v_s	51.7
Desorption					
0.921	3.79	0.910	43.9	0.892	49.6
0.853	3.20	0.825	41.5	0.815	48.3
0.759	2.71	0.746	39.1	0.737	45.8
0.665	2.45	0.665	36.8	0.662	41.9
0.568	2.09	0.573	34.4	0.578	37.4
0.475	1.78	0.484	32.0	0.488	34.4
0.372	1.36	0.438	28.8	0.457	27.8
0.275	1.22	0.428	24.6	0.375	22.9
		0.329	20.8	0.275	20.0
		0.230	17.9	0.181	17.2
		0.137	15.2		

TABLE R

PORE VOLUME DISTRIBUTION FOR BENZENE-DRIED MATERIALS
AS DETERMINED FROM NITROGEN ADSORPTION DATA

Chlorite Holocellulose		KOH-extracted Chlorite Holocellulose	
Pore Diameter, A.	Relative Pore Volume	Pore Diameter, A.	Relative Pore Volume
8.0	0.34	8.0	0.25
16.0	1.37	16.0	1.10
24.0	2.36	24.0	2.05
27.0	2.61	30.0	2.62
30.0	2.80	33.0	2.79
33.0	2.89	36.0	2.90
36.0	2.94	38.0	2.99
40.0	2.94	42.0	3.01
44.0	2.83	46.0	2.98
50.0	2.55	50.0	2.87
60.0	2.01	60.0	2.44
70.0	1.49	70.0	1.95
80.0	1.08	80.0	1.48
90.0	0.81	90.0	1.11
100.0	0.64	100.0	0.83
110.0	0.53	110.0	0.63
120.0	0.47	120.0	0.50

TABLE S

EFFECT OF ADSORBED WATER ON THE AREA OF BENZENE-DRIED, KOH-EXTRACTED CHLORITE HOLOCELLULOSE

Moisture Regained, percentage of ovendry weight	B.E.T. Area, sq. m./g.
0.0	67.0
5.2	24.3
9.6	5.31
16.4	1.06
20.0	0.86
27.7	0.78
31.5	0.75
Original water-dried area	0.64